PB84-234657

Overview of 'Who Is Doing What' in Laboratory- and Bench-Scale Hazardous Waste Incineration Research

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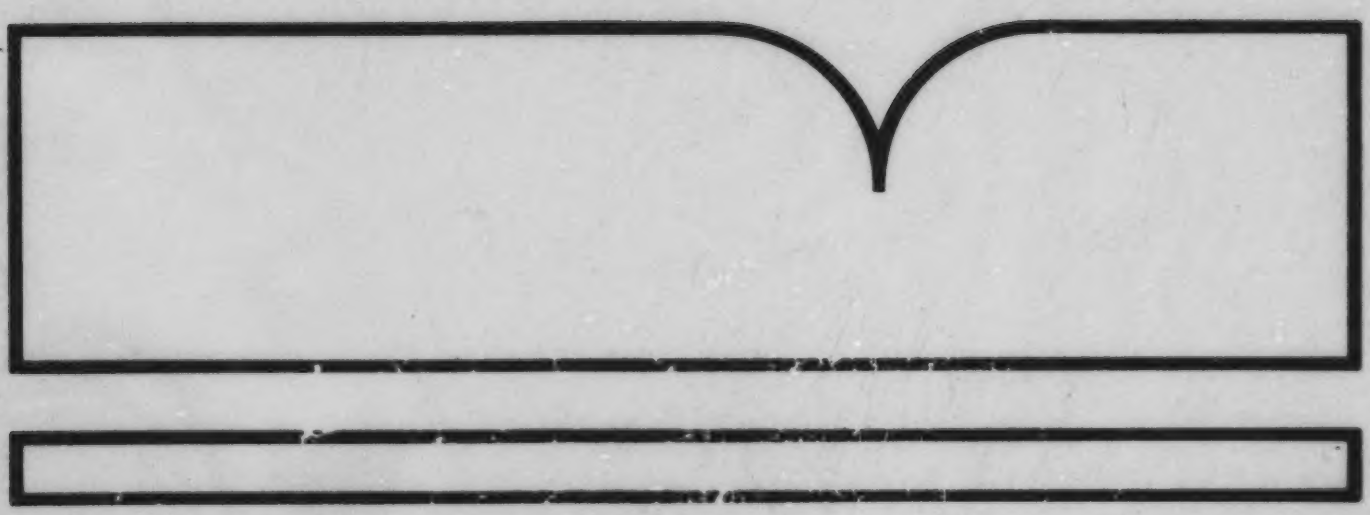
Cincinnati, OH

Aug 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-234657

EPA-600/D-84-209
August 1984

AN OVERVIEW OF "WHO IS DOING WHAT" IN LABORATORY- AND BENCH-SCALE HAZARDOUS WASTE INCINERATION RESEARCH

by

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INFORMATION SERVICE
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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/D-84-209	2.
3. RECIPIENT'S ACCESSION NO. PB84 234657	
4. TITLE AND SUBTITLE An Overview of "Who Is Doing What" In Laboratory- And Bench-Scale Hazardous Waste Incineration.	5. REPORT DATE August 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C.C. Lee and George L. Huffman	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS US EPA 26 West St. Clair St. Cincinnati, OH 45268	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS US EPA 26 West St. Clair St. Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This paper summarizes and compares five past and eight current research studies in the area of laboratory- and bench-scale hazardous waste incineration research. The subjects covered range from non-flame to turbulent flame thermal destruction, and from conventional to innovative incineration processes. As a conclusion, this paper provides:

- Information summarizing the thermal destruction testing results for various hazardous waste compounds.
- Recommendations regarding future directions in the area of hazardous/toxic waste thermal destruction research.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 111
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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AN OVERVIEW OF "WHO IS DOING WHAT" IN LABORATORY- AND BENCH-SCALE HAZARDOUS WASTE INCINERATION RESEARCH

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INTRODUCTION

It was estimated that 57 million tons of organic hazardous/toxic wastes are generated annually in the United States, and 90 percent of them are disposed of by environmentally unsound methods, thus posing a serious threat to human health and the environment[1]. The Federal government responded to the critical hazardous waste problem with the enactment of the Resource Conservation and Recovery Act (RCRA) in 1976 (Public Law 94-580), Toxic Substance Control Act (TSCA) in 1976 (Public Law 94-469), and a comprehensive "Superfund" program in 1980 (Public Law 96-510) to assure the reliable management of hazardous/toxic waste disposal operations and dump site clean-up. The enactment of these Laws has intensified research into the thermal destruction of organic chemical waste and this research has accumulated a large amount of useful information.

This paper describes the past and current efforts in the area of small-scale research that has come about due to the passage of RCRA and TSCA. The purpose of this paper is to provide information relative to "who is doing what" for the hazardous waste management industry in terms of generating research information and in planning future programs. This paper covers the following research activities:

▲ Past Research Activities Including:

- Non-flame Thermal Decomposition Research by the University of Dayton Research Institute (UDRI) [though some of this research is still ongoing --- see below]
- Non-flame Thermal Decomposition Research by the Union Carbide Corporation
- Laminar Flame Combustion of Chlorinated Hydrocarbons by the Illinois Institute of Technology
- Flame-Mode Hazardous Waste Thermal Destruction Research by the Energy and Environmental Research Corporation (EERC)
- Thermal Destruction of Chlorophenol Residues by Environment-Canada

▲ Current Research Activities Including:

- Hazardous Waste Incineration Engineering Analysis
- EPA In-House Research
- Investigation of Gas-Phase Thermal Decomposition Properties of Hazardous Organic Compounds by UDRI
- The Incineration Characteristics of Selected Chlorinated Hydrocarbons by the Louisiana State University
- Non-flame Waste Decomposition of Hazardous Waste by the Midwest Research Institute
- Heterogeneous Catalytic Oxidation of Model Chlorinated Hydrocarbons by the Massachusetts Institute of Technology

- Oxidation of Model Waste Components in Supercritical Water by the Massachusetts Institute of Technology
- Molecular Beam Mass Spectroscopic Study of Chlorinated Hydrocarbon Flames by the Illinois Institute of Technology

RESEARCH NEEDS

In 1980, EPA published a comprehensive list of hazardous wastes[2, 3, 4]. One year later (1981), under RCRA, EPA promulgated the standards for operating hazardous waste incinerators[5]. The key requirements of the standards are:

▲ An incinerator must achieve a Destruction and Removal Efficiency (DRE) of 99.99 percent for each Principal Organic Hazardous Constituent (POHC) designated for each waste feed.

Note: Initially, EPA suggested the use of compound incinerability and concentration for selecting POHCs. It further suggested that heat of combustion (ΔH_c) be used as the measure of compound incinerability in its guidance manual to permit writers[6]. Table 1 shows the heat of combustion of selected ("Appendix VIII") hazardous compounds.

TABLE 1

RANKING OF INCINERABILITY OF ORGANIC HAZARDOUS CONSTITUENTS FROM APPENDIX VIII, PART 261 ON THE BASIS OF HEAT OF COMBUSTION

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Trichloromonofluoromethane	0.11	1,1,1,2-Tetrachloroethane	1.39
Tribromomethane	0.13	1,1,2,2-Tetrachloroethane	1.39
Dichlorodifluoromethane	0.22	1,1-Dibromomethane	1.43
Tetrachloromethane (Carbon tetrachloride)	0.24	1,2-Dibromo-3-chloropropane	1.48
Tetranitromethane	0.41	Pentachloronitrobenzene	1.62
Hexachloroethane	0.46	Bromomethane	1.70
Dibromomethane	0.50	Dichloromethane	1.70
Pentachloroethane	0.53	Trichloroethane (Trichloroethylene)	1.74
Hexachloropropene	0.70	Hexachlorobenzene	1.79
Chloroform	0.75	Bis (chloromethyl) ether	1.97
Chloral (trichloroacetaldehyde)	0.80	1,1,1-Trichloroethane	1.99
Cyanogen bromide	0.81	1,1,2-Trichloroethane	1.99
Trichloromethanetiol	0.84	Pentachlorobenzene	2.05
Hexachlorocyclohexane	1.12	Pentachlorophenol	2.09
Tetrachloroethane (Tetrachloroethylene)	1.19	Hexachlorocyclopentadiene	2.10
Cyanogen chloride	1.29	Hexachlorobutadiene	2.12
Formic acid	1.32	Kepone	2.15
Iodomethane	1.34	2,3,4,6-Tetrachlorophenol	2.23
Tetrachloroethane, N.O.S.	1.39	Dichlorophenylarsine	2.31

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituents	Heat of Combustion kcal/gram
Decachlorobiphenyl	2.31	2,4,6-Trichlorophenol	2.88
Endosulfan	2.33	N-Nitroso-N-methylurea	2.89
Nonachlorobiphenyl	2.50	Heptachlorobiphenyl	2.98
Toxaphene	2.50	1,1-Dichloroethane	3.00
1,2,4,5-Tetrachlorobenzene	2.61	1,2-Dichloroethane	3.00
Bromoacetone	2.66	trans-1,2-Dichloroethane	3.00
Dichloroethylene, N.O.S.	2.70	Phenyl dichloroarsine	3.12
1,1-Dichloroethylene	2.70	N-Nitrosoarcosine	3.19
Chlordane	2.71	Azaserine	3.21
Heptachlor epoxide	2.71	2-Fluoroacetamide	3.24
Phenylmercury acetate	2.71	Chloromethane	3.25
Octachlorobiphenyl	2.72	Hexachlorobiphenyl	3.28
Acetyl chloride	2.77	Bis (2-chloroethyl) ether	3.38
Trichloropropane, N.O.S.	2.81	1,2,3,4,10,10-Hexachloro-1,4,4a,5,7,8a,	3.38
1,2,3-Trichloropropane	2.81	hexahydro-1,4:5,8-endo, endo-	
Dichloropropanol, N.O.S.	2.84	dimethanonaphthalene	
Dimethyl sulfate	2.86	Benzenearsonic acid	3.40
2,4,5-T	2.86	Maleic anhydride	3.40
2,4,5-Trichlorophenol	2.88	1,2,4-Trichlorobenzene	3.40

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
TCDD	3.43	Dichloropropane, N.O.S.	3.99
Dichloropropene, N.O.S.	3.44	1,2-Dichloropropane	3.99
1,3-Dichloropropene	3.44	Methylparathion	4.00
Endrin	3.46	Uracil mustard	4.00
Chloromethyl methyl ether	3.48	Amitrole	4.01
2,4-Dinitrophenol	3.52	Dimethoate	4.02
Nitrogen mustard N-oxide and hydrochloride salt	3.56	Tetraethyl lead	4.04
Parathion	3.61	4,6-Dinitro-o-cresol and salts	4.06
2,4-D	3.62	N-Methyl-N-nitro-N-nitroguanidine	4.06
Pentachlorobiphenyl	3.66	Mustard gas	4.06
1,3-Propane sultone	3.67	Maleic hydrazide	4.10
Methyl methanesulfonate	3.74	Dinitrobenzene, N.O.S.	4.15
Aldrin	3.75	N-Nitroso-N-methylurethane	4.18
Nitroglycerine	3.79	1,4-Dichloro-2-butene	4.27
2,4-Dichlorophenol	3.81	Nitrogen mustard and hydrochloride salt	4.28
2,6-Dichlorophenol	3.81	Tetrachlorobiphenyl	4.29
Hexachlorophene	3.82	Hydrazine	4.44
Trypan blue	3.84	Vinyl chloride	4.45
Benzotrichloride	3.90	Formaldehyde	4.47
Cycasin	3.92	Saccharin	4.49
N-Nitroso-N-ethylurea	3.92	3-Chloropropionitrile	4.50
Cyclophosphamide	3.97	DDT	4.51

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Thiourea	4.51	Dichloromethylbenzene	5.09
1-Acetyl-2-thiourea	4.55	Trichlorobiphenyl	5.10
Thiosemicarbazide	4.55	DDD	5.14
Dichlorobenzene, N.O.S.	4.57	Dimethylnitrosoamine	5.14
Ethyl cyanide	4.57	N-Nitrosodimethylamine	5.14
Bis (2-chloroethoxy) methane	4.60	Diethylarsine	5.25
2,4-Dinitrotoluene	4.68	Phthalic anhydride	5.29
Isocyanic acid, methyl ester	4.69	1-(o-chlorophenyl) thiourea	5.30
7-Oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid	4.70	1-Methyl-2-(methylthio)propionaldehyde-o-(methylcarbonyl) oxime	5.34
Ethyl carbamate	4.73	2-sec-Butyl-4,6 dinitrophenol (DNBP)	5.46
5-(Aminomethyl)-3-isoxazolol	4.78	p-Nitroaniline	5.50
Methylthiouracil	4.79	Chlorobenzilate	5.50
4,4'-Methylene-bis-(2-chloroaniline)	4.84	Dieldrin	5.56
Bis (2-chloroisopropyl) ether	4.93	2,4,5-TP	5.58
4-Nitrophenol	4.95	Methoxychlor	5.59
DDE	5.05	4-Nitroquinoline-1-oxide	5.59
Dimethylcarbamoyl chloride	5.08	Diallate	5.62
p-Chloro-m-cresol	5.08	Daunomycin	5.70

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Ethylenebisdithiocarbamate	5.70	Malononitrile	5.98
3,3'-Dichlorobenzidine	5.72	5-Nitro-o-toluidine	5.98
Pronamide	5.72	Nitrobenzene	6.01
Aflatoxins	5.73	3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol	6.05
Disulfoton	5.73		
4,6-Dinitrophenol	5.74	Benzoquinone	6.07
Diepoxybutane	5.74	N-Nitrosomethylethylamine	6.13
Dimethyl phthalate	5.74	p-Chloroaniline	6.14
Glycidylaldehyde	5.74	Benzyl chloride	6.18
Acrylamide	5.75	Resorcinol	6.19
3,3-Dimethyl-1-(methylthio)-2-butanone-o-(methylamino)carbonyl oxime	5.82	Propylthiouracil	6.28
		Paraldehyde	6.30
4-Bromophenyl phenyl ether	5.84	Dichlorobiphenyl	6.36
Thiuram	5.85	Diethyl phthalate	6.39
Methanethiol	5.91	Dioxane	6.41
Tolylene diisocyanate	5.92	2-Methyllactonitrile	6.43
Chloroambucil	5.93	N-Nitrosopyrrolidone	6.43
Thioacetamide	5.95	Methyl methacrylate	6.52
Ethylenethiourea	5.98	Chlorobenzene	6.60

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
o-Toluidine hydrochloride	6.63	Phenacetin	7.17
N,N-Bis-(2-chloroethyl)-2-naphthylamine	6.64	Ethyl methacrylate	7.27
2,6-Dinitrotoluene di-n-octyl phthalate	6.67	Di-n-butyl phthalate	7.34
Reserpine	6.70	3,3'-Dimethoxybenzidine	7.36
Methyl hydrazine	6.78	Acetonitrile	7.37
Cyanogen	6.79	4-Aminopyridine	7.37
Ethylene oxide	6.86	2-Chloronaphthalene	7.37
N-Nitrosodiethylamine	6.86	2 Propyn-1-ol	7.43
2-Chlorophenol	6.89	1-Naphthyl-2-thiourea	7.50
N-Phenylthiourea	6.93	Isosafrole	7.62
Acrolein	6.96	Dihydrosafrole	7.66
2-Butanone peroxide	6.96	Safrole	7.68
p-Dimethylaminoazobenzene	6.97	Auramine	7.69
1,4-Naphthoquinone	6.97	Crotonaldehyde	7.73
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts	7.00	Allyl alcohol	7.75
		Monochlorobiphenyl	7.75
N-Nitrosodiethanolamine	7.02	Phenol	7.78
N-Nitrosopiperidine	7.04	Phenylenediamine	7.81
N-Nitrosonornicotine	7.07	2-Acetylaminofluorine	7.82

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Di-n-propylnitrosoamine	7.83	N-Nitrosodi-N-butylamine	8.46
Acrylonitrile	7.83	2,4-Dimethylphenol	8.51
Di-n-propylnitrosoamine	7.83	Indenol (1,2,3-c,d) pyrene	8.52
Ethyleneimine	7.86	Diethylstilbestrol	8.54
1,1-Dimethylhydrazine	7.87	1-Naphthylamine	8.54
1,2-Dimethylhydrazine	7.87	2-Naphthylamine	8.54
N-Nitrosomethylvinylamine	7.91	Methacrylonitrile	8.55
Pyridine	7.93	Isobutyl alcohol	8.62
Methapyrilene	7.93	1,2-Diethylhydrazine	8.68
Strychnine and salts	8.03	1-Picoline	8.72
Methyl ethyl ketone (MEK)	8.07	Aniline	8.73
Cresylic acid	8.09	1,2-Diphenylhydrazine	8.73
Cresol	8.18	3,3'-Dimethoxybenzidine	8.81
Toluene diamine	8.24	7H-Dibenzo (c,g) carbazole	8.90
Acetophenone	8.26	Benz (c) acridine	8.92
Butyl benzyl phthalate	8.29	Nicotine and salts	8.92
Ethyl cyanide	8.32	4-Amino biphenyl	9.00
Bis (2-ethylhexyl) phthalate	8.42	Diphenylamine	9.09
Benzenethiol	8.43	2-Methylaziridine	9.09

TABLE 1 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Constituent	Heat of Combustion kcal/gram
Benzidine	9.18	Dibenz (a,h) acridine	9.53
Benzo (b) fluoranthene	9.25	Dibenz (a,j) acridine	9.53
Benzo (j) fluoranthene	9.25	alpha, alpha-Dimethylphenethylamine	9.54
Benzo (a) pyrene	9.25	3-Methylcholanthrene	9.57
Dibenzo (a,e) pyrene	9.33	n-Propylamine	9.58
Dibenzo (a,h) pyrene	9.33	7,12-Dimethylbenz (a) anthracene	9.61
Dibenzo (a,i) pyrene	9.33	Naphthalene	9.62
Fluoranthene	9.35	Benzene	10.03
Benz (a) anthracene	9.39	Toluene	10.14
Dibenz (a,h) anthracene (Dibenzo (a,h) anthracene)	9.40		

- An incinerator burning hazardous waste containing more than 0.5 percent chlorine must remove 99 percent of the hydrogen chloride from the exhaust gas.

- An incinerator burning hazardous waste must not emit particulate matter exceeding 180 milligrams per dry standard cubic meter.

A trial burn test(s) is required to demonstrate the ability of a hazardous waste incinerator to comply with the above performance standards.

In 1979, under TSCA, EPA promulgated the standards for operating PCB (Polychlorinated Biphenyl) incinerators. The general requirements of the standards are[7]:

- Liquid PCB's - Maintenance of the introduced liquids for a 2-second dwell time at 1200°C (± 100°C) and 3 percent excess oxygen in the stack gas; or
- Maintenance of the introduced liquids for a 1 1/2 second dwell time at 1600°C (± 100°C) and 2 percent excess oxygen in the stack gas.
- Combustion efficiency shall be at least 99.9 percent computed as follows:

$$\text{Combustion efficiency} = C_{CO_2}/(C_{CO_2} + C_{CO}) \times 100$$

where

C_{CO_2} = Concentration of carbon dioxide

Cco = Concentration of carbon monoxide

- Non-liquid PCBs - The mass of emissions from the incinerator shall be no greater than 0.001g PCB/kg of the PCB introduced into the incinerator. (This is equivalent to 99.9999% DRE).

- Similar to the RCRA requirements, a trial burn test(s) is required to demonstrate that the incinerator meets the above standards.

It has been well recognized that the destruction of hazardous materials by incineration is very effective, because it only takes seconds to destroy what might otherwise take months or years to degrade in a landfill site. However, incineration processes may pose significant risks from the inherent problems associated with incineration itself.

For example;

- How can the 99.99% DRE (in the case of a RCRA-bound incinerator) be effectively maintained?

- How can Principal Organic Hazardous Constituents be selected?

- And, perhaps most importantly, how can combustion by-products, or products of incomplete combustion, be controlled at safe levels?

Dealing with these problems requires full understanding of thermal destruction phenomena. Only on the basis of this full understanding can incineration regulations be realistically developed, and can incinerator controls be properly designed. This is why major research in incineration is needed.

In conducting its incineration research program, EPA's Industrial Environmental Research Laboratory in Cincinnati, Ohio has set the following major research goals. All of its research efforts are aimed at achieving these goals.

- ASSESSING CURRENT CAPABILITIES OF DESTRUCTORS

  To assess the performance capabilities (Destruction and Removal Efficiencies --- DREs etc.) of existing hazardous waste thermal destruction devices (incinerators, kilns, boilers, etc.) as the technical foundation for Agency policies and regulations with respect to thermal destruction as a hazardous waste disposal option.

▲ DEFINING POHCs and PICs

To provide the necessary scientific basis: (1) for selecting the appropriate Principal Organic Hazardous Constituents (POHCs) for specification in permits; and (2) for delineating those conditions of operation required to prevent the formation of hazardous Products of Incomplete Combustion (PICs).

▲ UNDERSTANDING THE THERMAL DESTRUCTION PROCESS

To develop an adequate understanding of thermal destruction chemistry and the engineering of thermal processes so as to be able to: (1) characterize and assess the performance of full-scale thermal destruction devices from a minimum set of evaluative tests; and (2) extrapolate performance information from one waste type to another or from one scale or type of equipment to another (e.g., so that small-scale test burns can reliably be used in permitting decisions).

▲ MONITORING COMPLIANCE

To define easily monitored incinerator facility operating parameters (e.g., CO/THC ratio, CO/CO_2 ratio, etc.) which correlate with system performance (e.g., Destruction and Removal Efficiency, PIC formation, etc.) so as to allow rapid,

reliable and economical determination by enforcement officials of compliance with permit conditions and so as to define the necessary preventive and corrective actions to avoid uncontrolled excursions from permit conditions.

▲INNOVATIVE TECHNOLOGIES

To improve the cost-effectiveness and broaden the applicability of thermal processing as a hazardous waste disposal option.

PAST RESEARCH ACTIVITIES

Although combustion has been a subject of research for decades, previous work on the incineration of hazardous wastes has been minimal. In 1956, Garner, et al.[8] examined the inhibitory effects of chlorinated methanes on the burning velocities of propane/air mixtures when injected in quantities less than 1 mole percent. They concluded that the order of effectiveness in reducing burning velocity was $CH_4 < CH_3Cl < CH_2Cl_2 < CCl_4$. Fletcher[9] in 1968 measured the spatial velocities of chlorine/fluorine flames over the flammable range. The results were compared with the theoretical flame temperature, equilibrium compositions, and a simple plausible rate expression. He concluded that although the spatial velocities did not correlate well with either temperature or the simple rate expression, they did correlate with equilibrium fluorine atom concentration in the products.

Wolfhard[10,11] was probably the pioneer to study the flammabilities of substances. He used the oxygen index as the parameter to compare flammabilities of some light fuels. Fenimore[12] used the same concept to study the flammability of polymers and concluded that the oxygen index seemed to be a useful measurement of polymer flammability. It was easy, reproducible, and numerical.

Bernard, et al.[12,13,14,15] 1964 to 1968, studied the thermal oxidation of ketones. They concluded that oxidation of ketone-related compounds such as acetone, methyl-ethyl-ketone, and diethyl ketone followed the same pattern (i.e., that hydrogen abstraction could take place from the methyl group or from the α or β position of the alkyl group).

Since the early 1970's, the EPA has been developing R&D information and reports for public distribution concerning the state-of-the-art of industrial non-radioactive hazardous waste disposal via thermal degradation or incineration. Since 1976, the enactment of RCRA and later of TSCA has intensified the research of hazardous/toxic waste thermal disposal. The following summarizes the major recent research activities in laboratory- and bench-scale efforts.

Non-flame Thermal Decomposition Research

Under a series of contracts and grants with EPA's Industrial Environmental Research Laboratory-Cincinnati, the University of Dayton

Research Institute (UDRI) has been performing laboratory-scale studies of waste thermal oxidation characteristics in a non-flame environment since 1974[16,17,18,19,20,21,22].

▲Study Scope

- To investigate thermal decomposition properties of waste streams
- To evaluate the thermal decomposition behavior of principal organic hazardous constituents (POHCs)
- To observe the products of incomplete combustion (PICs)
- To determine the time and temperature effects on the gas phase oxidation of premixed, non-flame systems
- To investigate the role of oxygen concentration in thermal decomposition processes.

▲Study Approach

During their studies from 1974 to 1984, UDRI has developed four thermal instrumentation systems and tested numerous compounds. The four instrumentation systems are:

- Discontinuous Thermal Systems (DTS)
- Thermal Decomposition Analytical System (TDAS)
- Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) System
- Packaged Thermal Reactor System (PTRS)

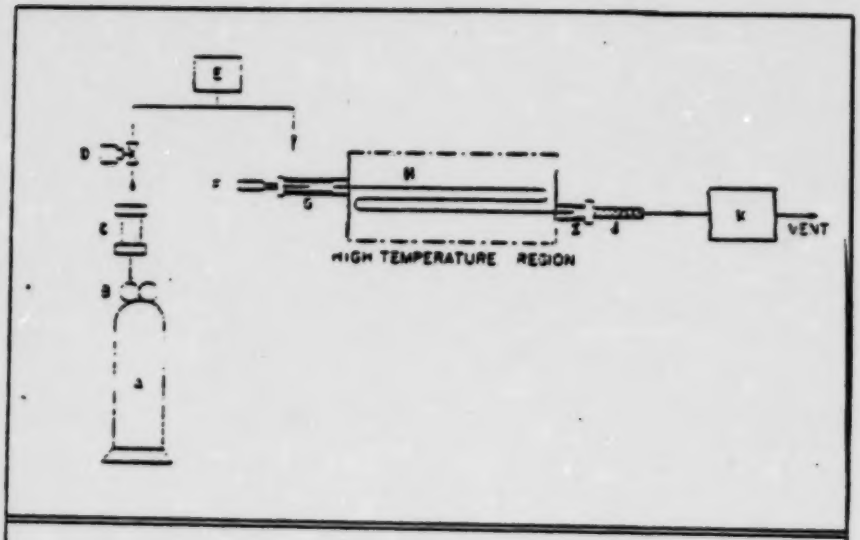
Compounds tested on these four systems have the following general attributes in common:

- Microgram quantities of test compounds investigated
- Non-flame environment
- Pure compounds premixed with air and some actual waste streams and mixtures tested
- Plug flow assumption.

General aspects of each of these 4 systems are outlined as follows:

System 1: Discontinuous Thermal System (DTS)

In 1974[17], UDRI developed the first system, the Discontinuous Thermal System (DTS), to study the thermal decomposition properties of pesticides. A schematic of the thermal reactor portion of this system is shown in Figure 1. The system involved a folded, high-temperature, small-bore, quartz tube reactor and a gas chromatograph. The quartz tube was placed in a Lindberg furnace and had an effective length of 84 cm. and



A COMPRESSED AIR, BREATHING QUALITY GRADE
B TWO-STAGE PRESSURE REGULATOR
C "HYDROPURGE" FILTER
D FLOW CONTROL VALVE
E PRESSURE TRANSDUCER
F SAMPLE HOLDER, PYREX
G HEATED INLET CHAMBER
H QUARTZ TUBE
I HEATED OUTLET CHAMBER
J EFFLUENT TRAP, TENAX-GC OR CHARCOAL
K FLOW METER

Figure 1. Schematic of the discontinuous thermal system.

volume of 0.4 cm^3. During an experiment, a sample was gradually vaporized in a continuously flowing carrier gas such as air. The gaseous organic mixture was then passed through the heated quartz tube thermal reactor. The high molecular weight combustion products were then captured by an adsorptive trap after leaving the reactor. The trap was then removed from the DTS and installed in a programmed temperature gas chromatograph for the analyses of effluent products.

Several compounds such as Kepone, Mirex, and DDT were tested on this system. It was found that Mirex was the most thermally stable of the three pesticides. Kepone was slightly more thermally stable than the DDT. All of the chemicals were essentially destroyed at a residence time of about one second at temperatures between 500 and 700°C depending on the chemicals. Figure 2 shows the thermal destruction of the three pesticides[16].

In using this system, only low volatility samples could be tested. Although some PIC (products of incomplete combustion) work was done, the scope was limited, because of analytical considerations.

System 2: Thermal Decomposition Analytical System (TDAS)

To improve DTS-type testing, UDRI developed the TDAS in 1977[17]. A block diagram of TDAS is shown in Figure 3. The TDAS was able to handle gases, liquids, solids, polymers, and complex organic mixtures. The

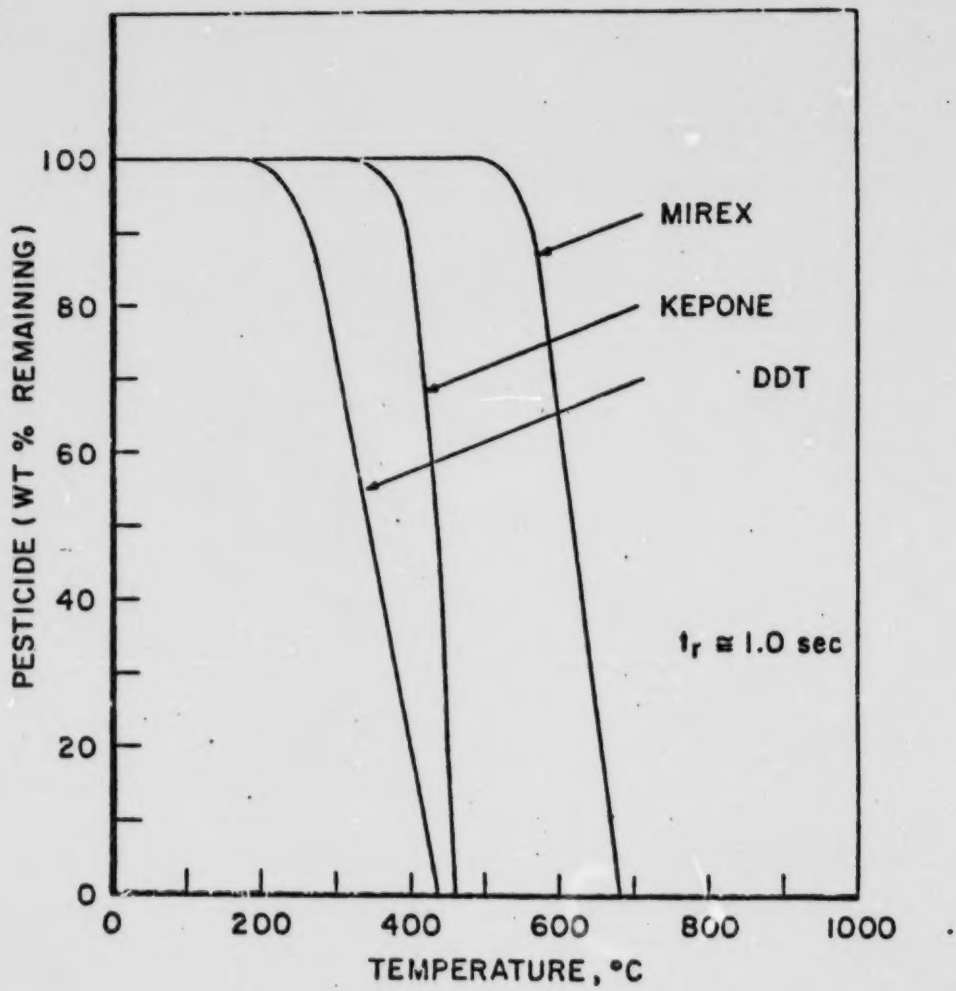


Figure 2. Comparison of the thermal destruction of three pesticides.

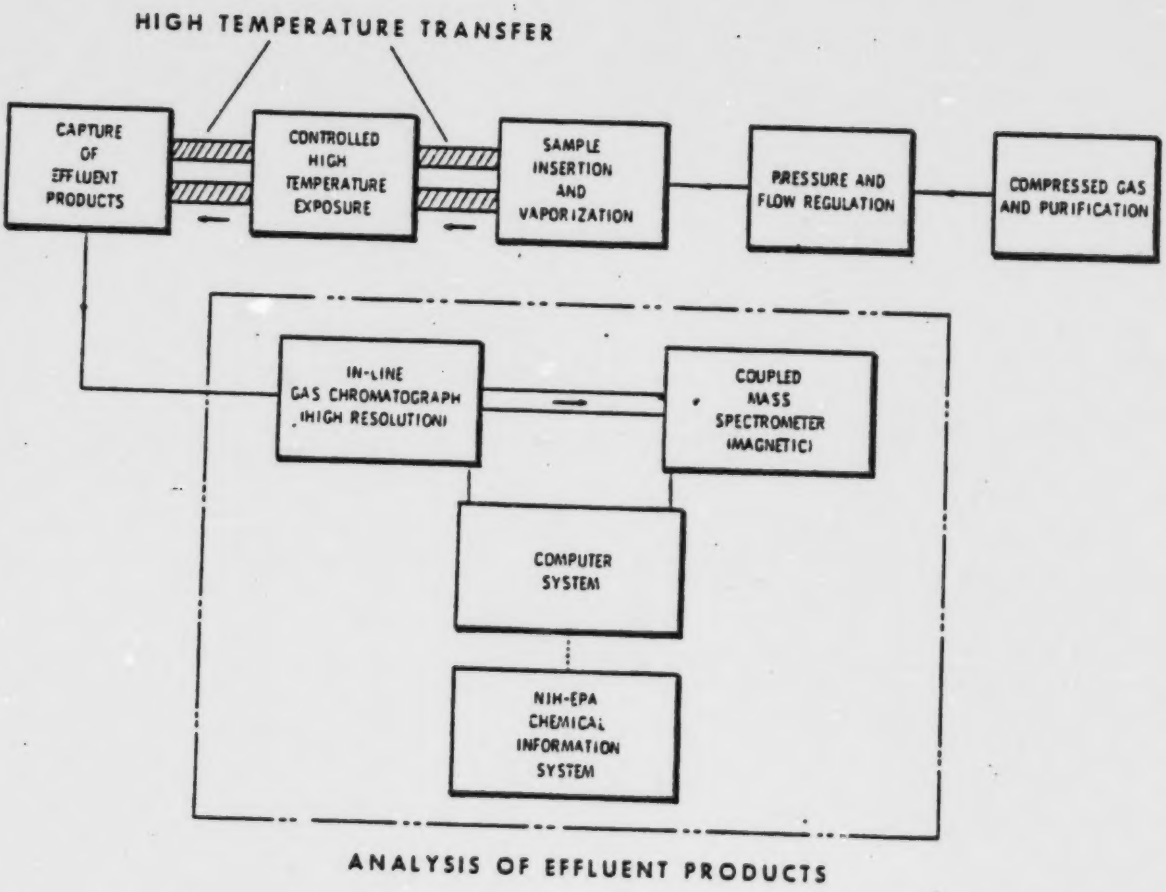


Figure 3. Block diagram of the TDAS.

quartz-tube temperature could be varied from 200 to 1150°C within ± 2°C. Among the major changes from the DTS were the following:

- Increased sample handling capability
- Improved quartz-tube reactor configuration (race-track shape, 3.5 turns, 0.97 mm ID by 980 mm length, 0.7 cm^3 volume)
- Cryogenic and adsorption trapping of organic effluent products
- Analysis of organic effluent products with a gas chromatograph-mass spectrometer and dedicated computer system.

Figure 4 presents a TDAS testing example of the relationship between the thermal decomposition of pentachloronitrobenzene and the formation and eventual decomposition of an associated PIC (hexachlorobenzene). This example is typical of the type of analyses commonly conducted using the TDAS[17]. Using the DTS and the TDAS, UDRI published a report in 1977[18] and a paper[19] covering the thermal oxidation destruction characteristics of the following compounds:

- Biphenyl
- Decachlorobiphenyl
- Dibenzo-p-dioxin
- Dibenzofuran
- Hexachlorocyclopentadiene (HCCP)

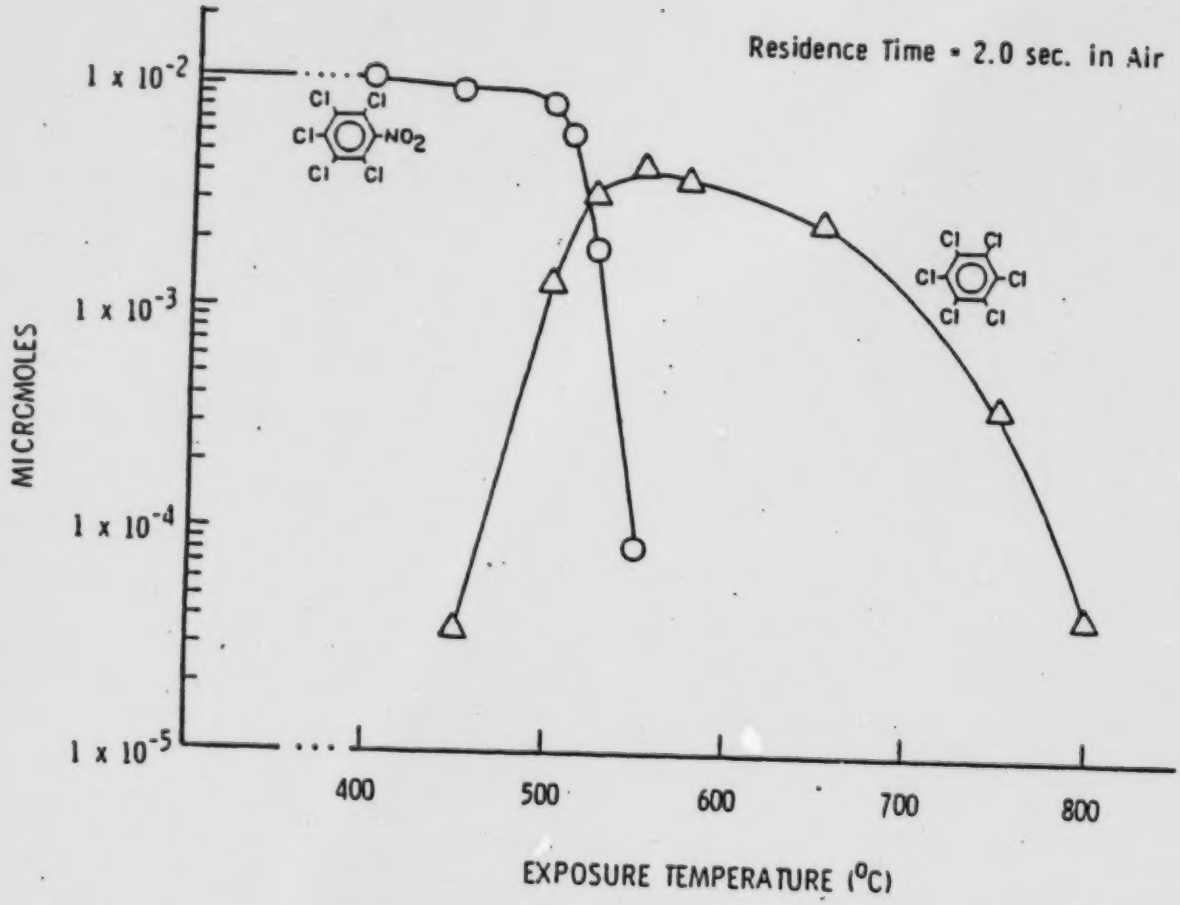


Figure 4. Thermal decomposition profile of pentachloronitrobenzene and its PIC (hexachlorobenzene).

- Hexachlorobenzene
- Octachlorocyclopentene (OCCP)
- Pentachlorobenzene
- Pentachlorobiphenyl
- Polychlorinated biphenyls (PCB)
- Tetrachlorobiphenyl

The TDAS was a powerful tool for studying the thermal decomposition of organic materials. It was a sophisticated instrumentation assembly because it incorporated GC-MS and a dedicated minicomputer.

System 3: Thermal Decomposition Unit - Gas Chromatographic (TDU-GC) System

A block diagram of the TDU-GC system and its instrumentation assembly are shown in Figure 5[20]. According to UDRI, not only can the TDU-GC maintain the same precision level as the TDAS does, but also it can reduce cost considerably by replacing the GC-MS with a high resolution gas chromatograph.

Figure 6 shows an example of a TDU-GC thermal decomposition profile for chloroform and its associated PICs. Also, a series of thermal decomposition profiles obtained using the TDU-GC are shown in Figure 7 for hexachlorobenzene. The profiles obtained at 1.0, 2.0, 4.0, and 6.0 seconds are characterized by a "low" temperature region of no thermal

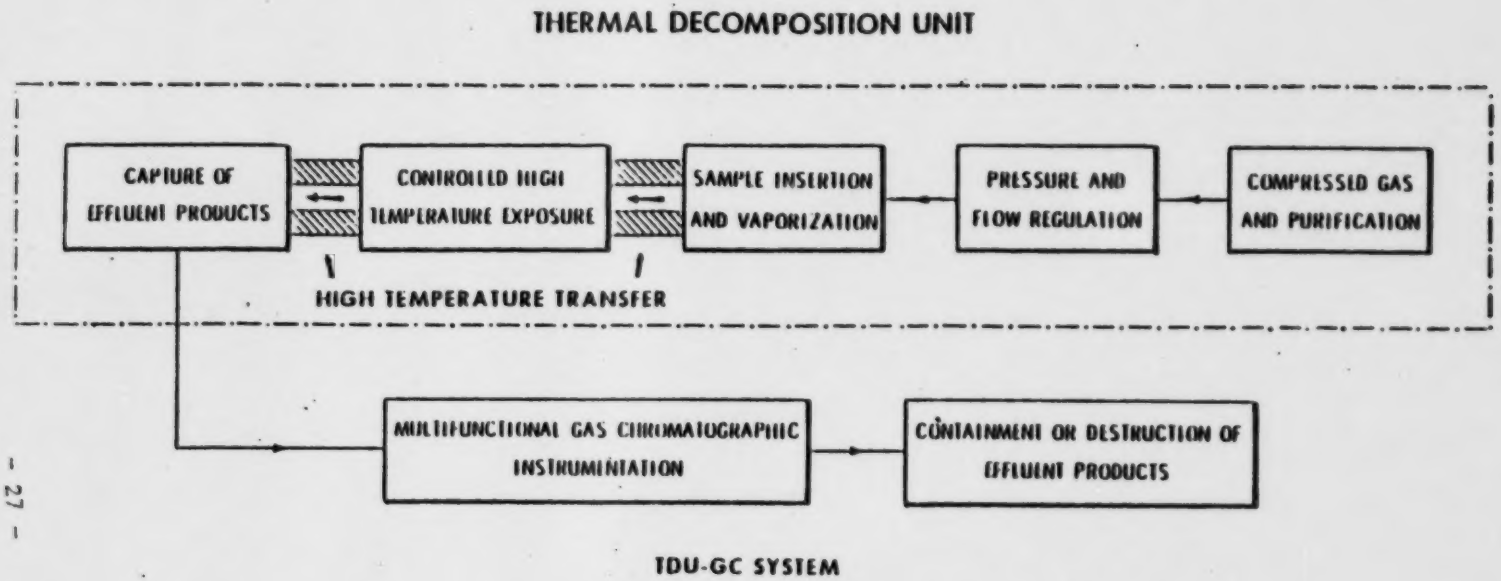


Figure 5. Block diagram of the TDU-GC system.

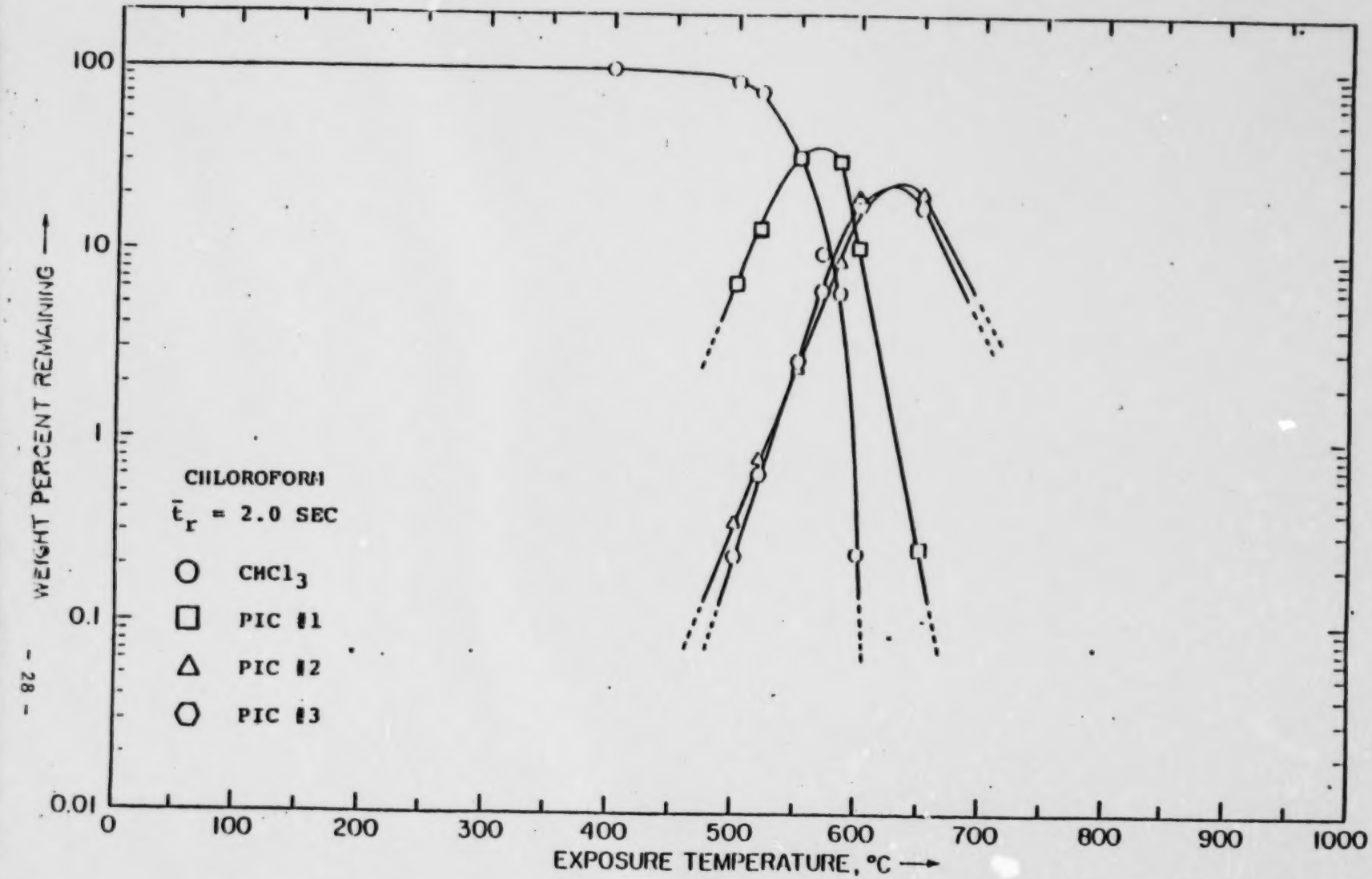


Figure 6. Thermal decomposition profile of chloroform.

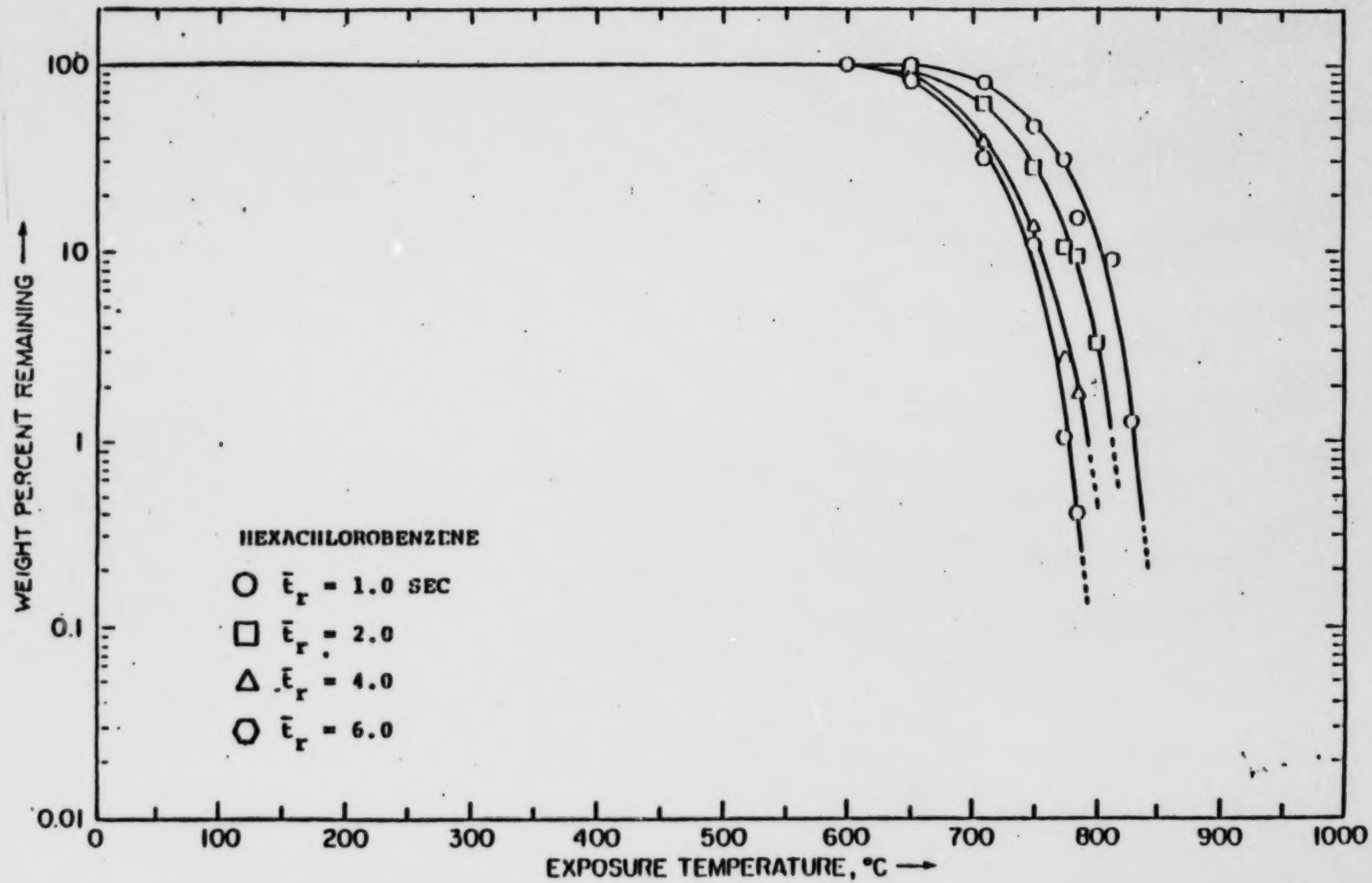


Figure 7. Thermal decomposition of hexachlorobenzene at various residence times.

decomposition, a region of onset of thermal decomposition, and a region of very rapid decomposition. Data of this type were utilized to establish kinetic rate parameters and to prepare a relative scale of incinerability of waste based on their calculated temperature for 99.99% destruction.

System 4: Packaged Thermal Reactor System (PTRS)

Based on the experience gained with the TDU-GC and comments from numerous researchers, UDRI developed the PTRS which was designed to be more rugged and versatile, compared to its predecessors. A schematic of the PTRS is shown in Figure 8. It is a three-channel unit with an internally mounted hydrogen flame ionization detector (HFID). The uniqueness of the PTRS is the use of dispersion chambers to generate the dilute sample inlet profiles.

▲ Study Conclusion

UDRI has prepared a report[22] documenting the findings of their previous research. They concluded that:

- Based on data generated in this most recent study of 20 test compounds and current understanding of chemical and physical phenomena occurring in an incinerator, the best available overall ranking scheme of destructibility of a hazardous waste is

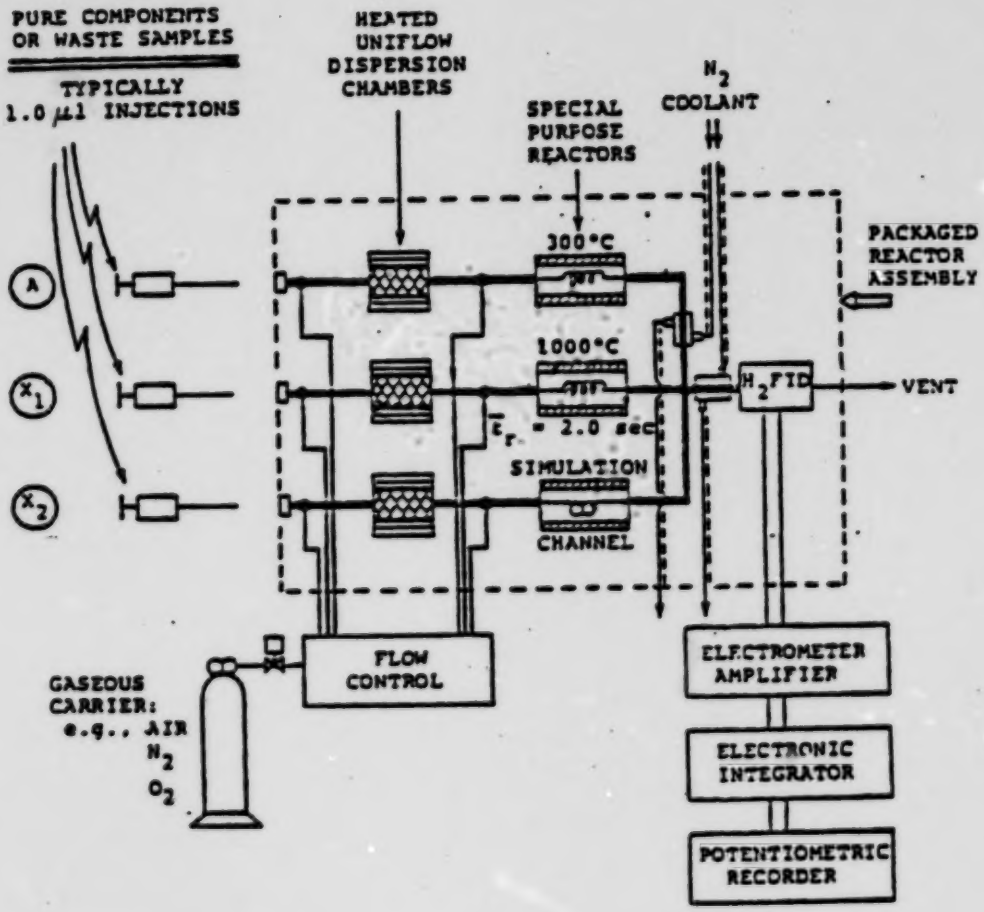


Figure 8. Schematic of the Packaged Thermal Reactor System.

laboratory-determined gas-phase thermal stability. The relative thermal stability of certain organic compounds can be explained and possibly predicted using fundamentals of organic chemistry and kinetics if the full range of decomposition mechanisms is considered.

- Numerous products of incomplete combustion were formed during the thermal decomposition of a majority of the compounds. These potential incineration products could have significant environmental impact and should be included in a complete assessment of the incinerability of a hazardous waste stream. Furthermore, identification of these products, which was not attempted because of time constraints, would be useful indicators of possible chemical reaction pathways.

- No single physical or chemical property of the test compounds is suitable as a ranking scheme for the entire list of 20 compounds.

- Compounds which are resistant to OH^- addition and whose weakest bond strength is large (>90 kcal/mole) will tend to be the most thermally stable.

- A pseudo-first order kinetic fit of the data is acceptable for describing the overall thermal decomposition behavior of the

test compounds. Such modeling is necessary for extrapolation of the data to other conditions. More thorough kinetic and mechanistic studies are necessary before these kinetic parameters should be used as an indication of the elementary reaction mechanism.

Non-flame Thermal Decomposition Research by Union Carbide Corporation (UCC)

▲Study Scope

- To determine fundamental time-temperature relationships for different chemicals (the relationships were described mathematically by kinetic rate equations)

- To develop a generalized relationship to predict kinetics for untreated chemicals

▲Study Approach

A sketch of the experimental set-up is shown in Figure 9. This set-up was a modification of the system used by the University of Dayton Research Institute[16]. The major modification was the manner in which the mixtures of experimental gases (test compounds) were inserted. UCC premixed the test compound with air and contained the mixtures in a cylinder,

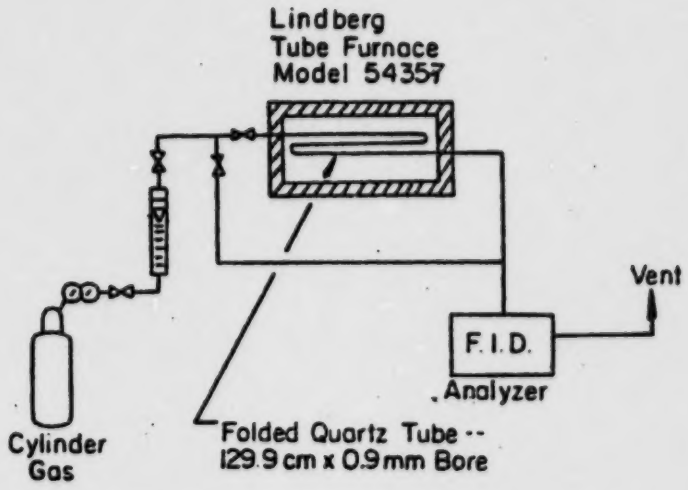


Figure 9. Oxidation apparatus.

while UDRI mixed the test compound with air when air was used as carrier gas to bring the test compound into the reactor. UCC claimed that their test compound had better mixing than that of UDRI's test compound.

In general, the set-up had a 0.9mm bore quartz tube (tube diameter was calculated from mercury displacement measurement). The quartz tube was twice folded at twelve-inch intervals so that 75 percent of its length of 130 centimeters could be located within the central portion of the furnace and within the limits of the flat temperature profile. The radial and longitudinal velocity and temperature gradients were minimized by the narrow bore, which allows conditions approaching a plug flow.

▲Study Conclusion

As a result, UCC published two papers. The first paper[23] discussed thermal oxidation kinetics of four chemicals: vinyl chloride, benzene, ethyl acrylate, and acrolein. The thermal oxidation data for all four chemicals was shown to fit a first-order kinetic rate model. The kinetic-rate model was then used to develop predictive equations for oxidation temperature and residence time requirements for a 99.9 percent destruction efficiency under different flow conditions. During the experiments, all compounds were run at 1000 ppm_v. Some of the compounds were run at 100 and 500 ppm_v and these runs gave good agreement with the 1000 ppm_v runs. The temperatures studied ranged from 800 to 1500°F and residence times from 0.1 to 2 seconds. Analyses were done for both specific chemicals and total hydrocarbons.

The second paper[24] discussed thermal oxidation kinetic data for 15 chemicals and also presented equations for predicting thermal oxidation destruction efficiencies based on molecular structure, residence time, and autoignition temperature. The predictive equations were developed from a multiple linear regression of the thermal oxidation data for the 15 chemicals. The two most important variables in the predictive equations were found to be autoignition temperature and residence time. The predictive equations are used to calculate the thermal oxidation temperature necessary to achieve a particular destruction and removal efficiency. Table 2 shows temperatures needed at different residence times by using the first-order kinetic model.

Laminar Flame Combustion of Chlorinated Hydrocarbons

Under an EPA Grant, Professor S.M. Senkan studied this subject first at the Massachusetts Institute of Technology and then at the Illinois Institute of Technology[25,26,27].

▲Study Scope

- To examine the combustion characteristics of various chlorinated hydrocarbon/methane/air flames

- To study burning velocities and carbon formation limits of various individual chlorinated methanes, ethanes, ethylenes, and chlorobenzene in mixtures with methane and air

Table 2. SUMMARY OF THERMAL OXIDATION KINETIC CONSTANTS[23,24]

Compound	A[a]	E[b] cal/g-mole	Auto-Ignition Temperature (°F)	Calculated Destruction Temperature from Eq. 4[c] $T_{99.99}$ at 1 sec. (°F)	$T_{99.99}$ at 2 sec. (°F)
Methane	1.68×10^{11}	52100	999	1542	1483
Ethane	5.65×10^{14}	63600	959	1368	1326
Propane	5.25×10^{19}	85200	871	1328	1298
Ethylene	1.37×10^{12}	50800	842	1323	1278
Propylene	4.63×10^{8}	34200	851	1318	1246
Butene	3.74×10^{14}	58200	723	1231	1197
Benzene	7.43×10^{21}	95900	1044	1350	1321
Toluene	2.28×10^{13}	56500	997	1337	1292
Acrolein	3.30×10^{10}	35900	453	1018	973
Ethanol	5.37×10^{11}	48100	793	1306	1256
Ethyl Acrylate	2.19×10^{12}	46000	721	1131	1090
Acrylonitrile	2.13×10^{12}	52100	898	1342	1296
Triethylamine	8.10×10^{11}	43200	450	1101	1059
Vinyl Chloride	3.57×10^{14}	63300	882	1373	1333
1,2-Dichloroethane	4.82×10^{11}	45600	775	1214	1174

(a) Frequency factor of Arrhenius equation
(b) Activation energy
(c) Assuming plug-flow reaction conditions

• To derive global and detailed combustion mechanisms, based on trichloroethylene (C_2HCl_3) premixed flame studies

▲ Study Approach

• Flame Velocity Study

Flame velocities were measured by using a quartz Bunsen burner with a diameter of 1.0 centimeters. Liquid chlorinated hydrocarbons (all of which were with at least 99.9% purity) were injected into metered and heated air/methane mixtures. When the desired flow/rates were set, and a stable, laminar flame was obtained, pictures were taken using an Olympus OM I camera and high-speed black and white film. Flame-front areas were then determined from the enlarged picture of the Bunsen cone using the cone-angle method[25].

Burning velocity is important because the square of it is proportional to the overall rate of combustion of the mixture.

Figure 10 shows that the burning velocities of chlorinated hydrocarbon systems decrease as the chlorine substitution of the molecule is increased.

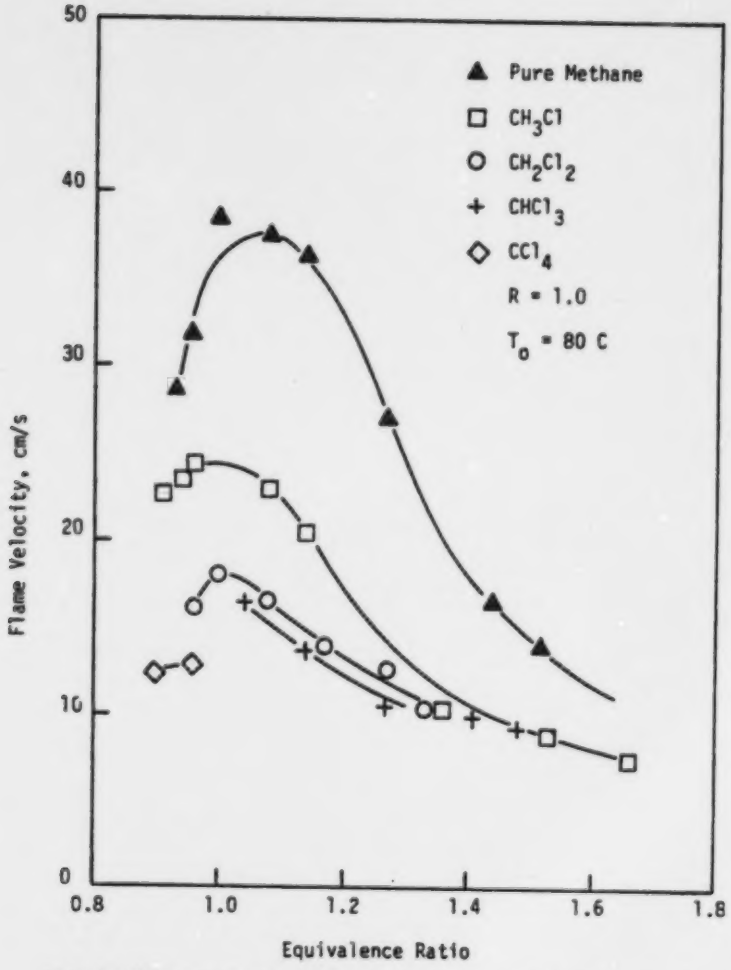


FIGURE 10. Flame velocities of chlorinated methane-methane-air mixtures.

• Carbon Formation Study

The apparatus for measuring carbon formation limits is shown in Figure 11[26b]. The liquid chlorinated hydrocarbons were injected into the pre-heated gases at a tee. The combustible mixture was then sent through a mixing chamber and through the burner assembly. The burner had a porous, sintered metal flame-holder with a heating coil inside, through which water at 80°C passed continuously. Thus the pre-mixed, pre-burned gases had been kept at a temperature in the range of 75-80°C throughout all the experiments. The nitrogen shield gas is to enclose the flame to minimize air diffusion from outside.

Carbon formation limits were determined visually, and were identified as the combustible mixture equivalence ratio at which the carbon luminosity was just suppressed. The so-called combustible mixture equivalence ratio is defined as the ratio of the actual fuel/oxygen ratio to the stoichiometric fuel/oxygen ratio, and the stoichiometric oxygen requirement is defined as the amount of oxygen needed to convert all the fuel carbon to CO_2 and to convert the fuel hydrogen (left over from the amount needed for HCl formation) to H_2O. Generally, carbon formation in premixed flames is not expected if the total oxygen is sufficient to convert the carbon to carbon monoxide. This, however, is the case assuming an equilibrium condition exists. In actual flames, carbon formation occurs more readily than might have been expected and varies from fuel to fuel.

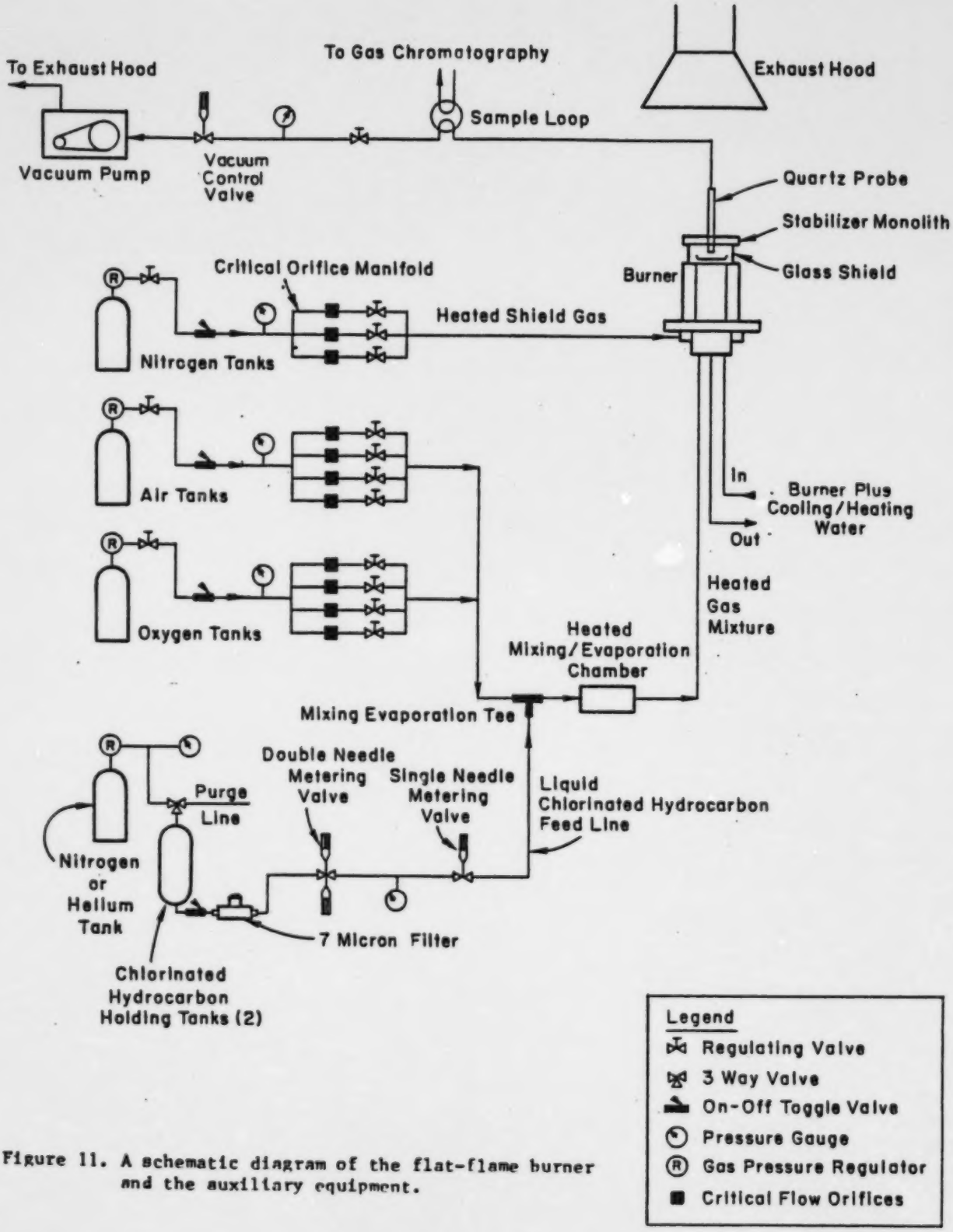


Figure 11. A schematic diagram of the flat-flame burner and the auxiliary equipment.

• Combustion Mechanism Studies

Chlorinated hydrocarbons (CHC) were found to undergo two-stage combustion reactions according to the following global mechanism:

First stage: $CHC + O_2 \longrightarrow CO, HCl, Cl_2$ Fast process

Second stage: $CO + O_2 \longrightarrow CO_2$ Slow process

HCl, Cl_2

inhibited

Trichloroethylene (C_2HCl_3) was used on the flat-flame burner (Figure 11) in discovering the two-stage combustion phenomena for chlorinated hydrocarbons. The major finding of this test is given in Figure 12[26]. This Figure reveals that the first stage reactions take place in a relatively narrow zone (of the order of 1-3mm), with a corresponding temperature increase of about 920°C. The first zone is then followed by the intermediate, "buffer" region of about 15 mm., in which the reaction rates and the temperature rise are relatively slow. Finally, the reaction rates increase again in the broader second reaction zone, with a temperature increase of about 500°C to a maximum of about 1500°C.

Figure 12 also shows that the oxidation of C_2HCl_3 is relatively fast, and that trichloroethylene essentially disappears completely on passing

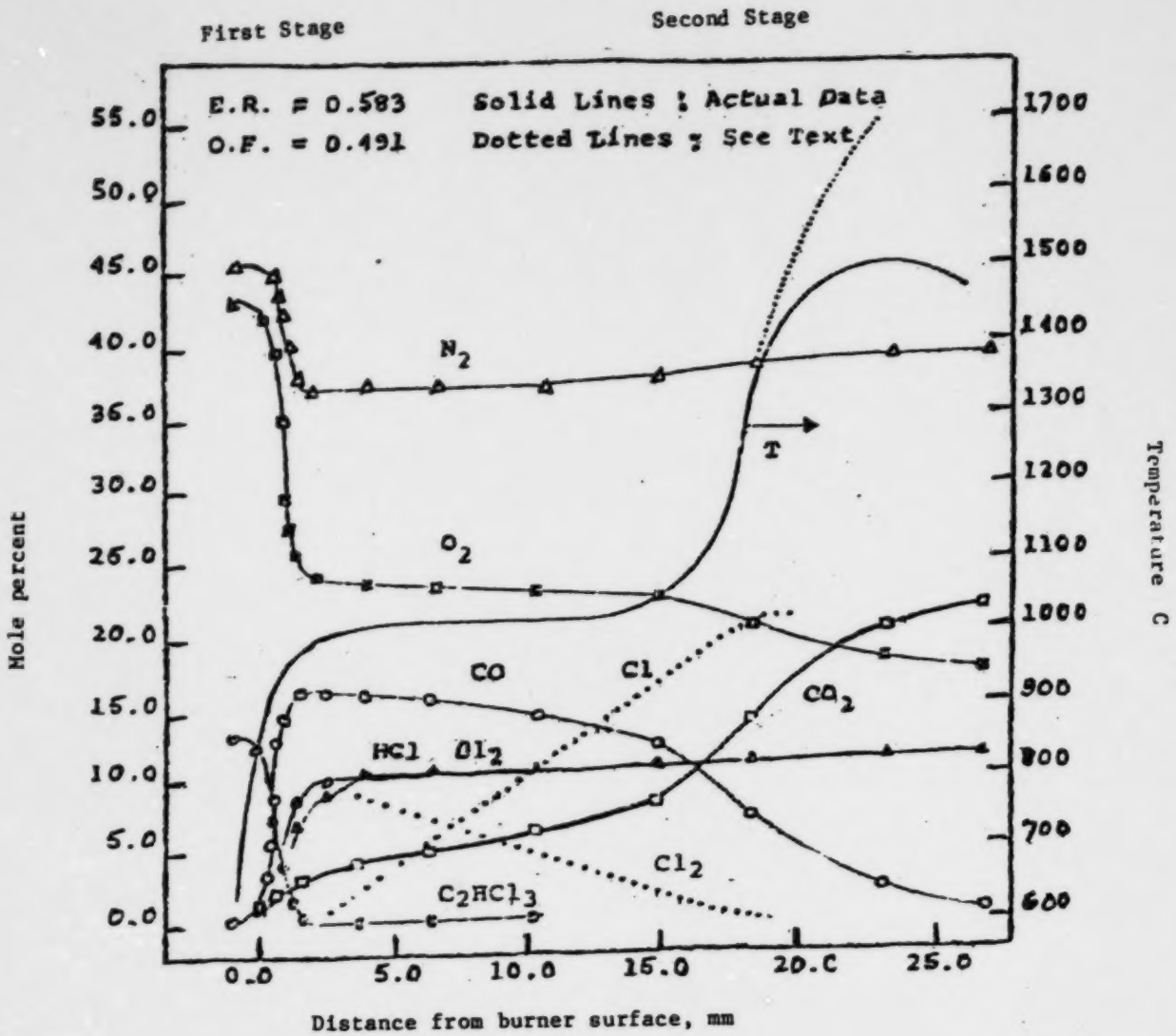


Figure 12. Profiles for the major species and the temperature.

through the first zone, with the simultaneous formation of CO as the principal product of incomplete combustion (PIC). Major chlorinated species that formed in the first stage, as a result of the oxidative decomposition of C_2HCl_3, were HCl and Cl_2. These profiles, therefore, indicate that HCl and Cl_2 are responsible for the slow oxidation of CO which dictates the behavior of the intermediate as well as the second stage flame zones. Consequently, the profiles shown in Figure 12 were used in proposing the two-state combustion model described above. The global model simplifies to the following for the first- and second-stage combustion in trichloroethylene flames:

First stage: $$C_2HCl_3 + O_2 \xrightarrow{\text{Fast}} 2\ CO + HCl + Cl_2 + 74\ \text{kcal.}$$

and the principal second-stage reaction involves the slow, HCl and Cl_2 inhibited oxidation of CO to CO_2 as shown below:

Second stage: $$2\ CO + O_2 \xrightarrow{\text{Slow}} 2\ CO_2 + 136\ \text{kcal}$$

The combustion of CO is inherently a slow reaction in the absence of hydrogen. However, if hydrogen is present, even trace quantities, the CO oxidation is strongly accelerated, principally due to the following fast reaction:

$$CO + OH\cdot \longrightarrow CO_2 + H\cdot$$

in which the OH· radicals act as a catalyst. The study also showed that hydrogen-catalyzed CO flames are strongly inhibited by chlorine and chlorine-bearing species. This inhibition is directly related to a decrease in the laminar burning velocity also.

The global model developed has a number of appropriate features. First, all reactions are exothermic as written, and the temperature can easily be related to the system equivalence ratio, the oxygen fraction of the O_2-N_2 mixture, and the H/Cl ratio of the CHC species. Second, the model also illustrates the increased/decreased inhibition of CO oxidation by the increased/decreased chlorine content of the CHCs by considering the H/Cl ratios of the chlorinated hydrocarbon systems. Since there is a stoichiometric relationship between the H and Cl content of a chlorinated hydrocarbon series, an increase in chlorine concentration is normally coupled with a simultaneous decrease in HCl concentration of CHC flames. Furthermore, since the heat of combustion of chlorinated hydrocarbon series decrease with increasing Cl substitution, inhibition due to decreases in the flame temperature are also implied in the above model.

For chlorinated hydrocarbons with sufficiently low chlorine contents (i.e. the H/Cl ratio is greater than one) such as CH_3Cl, C_2H_3Cl and C_6H_5Cl, the extent of CO inhibition will be small, so that their flames predominantly exhibit "single-stage" behavior.

▲Study Conclusion

This study concluded that the reason why it is difficult to incinerate chlorinated hydrocarbon wastes is not due to the stability of the CHC or the POHC molecules, but instead due to the slow combustion of their breakdown products namely the PICs. Detailed probe studies also revealed that a number of short-lived minor intermediates (PICs) such as other chlorinated hydrocarbons (CCl_4, C_2Cl_4 and $CHCl_3$), as well as carbonyl chloride ($COCl_2$) were observed. These intermediates formed and then decomposed to low concentration levels in a relatively narrow region. However, many of them persisted at trace concentration levels throughout the flame, indicating the potential for emissions problems in practical incineration/combustion systems.

Furthermore, the measurements of the CO concentration levels in the incinerator flue gases would be most suitable as an indicator for PIC and POHC emissions. That is, if significant CO emissions are not present, the presence of other carbon-based pollutants would be highly unlikely. Conversely, the presence of significant levels of CO in the combustion products would indicate that the conditions in the incinerator are improper and may result in POHC and other PIC emissions.

Flame-Mode-Hazardous Waste Thermal Destruction Research

Under an EPA contract, the Energy and Environmental Research Corporation (EERC) conducted a laboratory-scale study of flame-mode hazardous waste thermal destruction research during 1981-1982[28].

▲ Study Scope

- To examine methods of ranking hazardous waste incinerability
- To compare the differences between flame and non-flame waste destruction.

▲ Study Approach

- Summary of Existing Incinerability Ranking Procedures

  - Thermal Decomposition Kinetics: Under this approach, the thermal stability is assumed to be related to the dilute-phase non-flame thermal decomposition kinetic rate. This is measured in an experimental plug-flow reactor and reported as the temperature required to produce a 99.99% destruction efficiency (DE) over a specified residence time ($T_{99.99}$)[18,19,21,22,23].

- Autoignition Temperature (AIT): The AIT is used to determine the tendency of a compound to initiate combustion without the presence of an external ignition source. AIT has been found to correlate with thermal destruction data. The principal advantage to this approach is that AIT data are much more easily and rapidly obtained than thermal decomposition data and a much larger data base is presently available. If thermal stability is assumed to be measured by thermal decomposition kinetics, then AIT is proposed as an approach to estimating thermal stability.

- Heat of Combustion: This procedure was initially proposed because (1) increased chlorine substitution tends to yield higher thermal stability, as measured by $T_{99.99}$; and (2) heat of combustion tends to decrease with chlorine substitution. This yielded a potential relationship between heat of combustion and $T_{99.99}$[29].

- Property Correlation: Attempts have been made to generalize the results of the thermal decomposition experiments so that a ranking similar to the thermal decomposition ranking can be established without performing experiments[23,24]. The approach is to correlate $T_{99.99}$ with autoignition temperature and other compound-

specific physical and structural properties. The results have indicated that the strongest correlation is with autoignition temperature.

- Susceptibility to Radical Attack: Tsang and Shaub (30) have assumed that attack on the weakest compound bond by flame radicals is the process controlling destruction.

  The rankings are established by the grouping of compounds according to the bond most susceptible to radical attack.

• Microspray Reactor

The microspray reactor (Figure 13) was employed by EERC to investigate single-droplet thermal reactions without limitations associated with atomization, mixing, quenching or turbulent mixing. In this flame reactor, particles or droplets of the material to be studied were injected through a laminar, premixed, hydrocarbon flat flame and thermal decomposition of the material took place in a flame environment. The data from this testing were used for the following purposes:

- To determine what portion of the turbulent flame rankings were due to laminar flame and evaporation processes

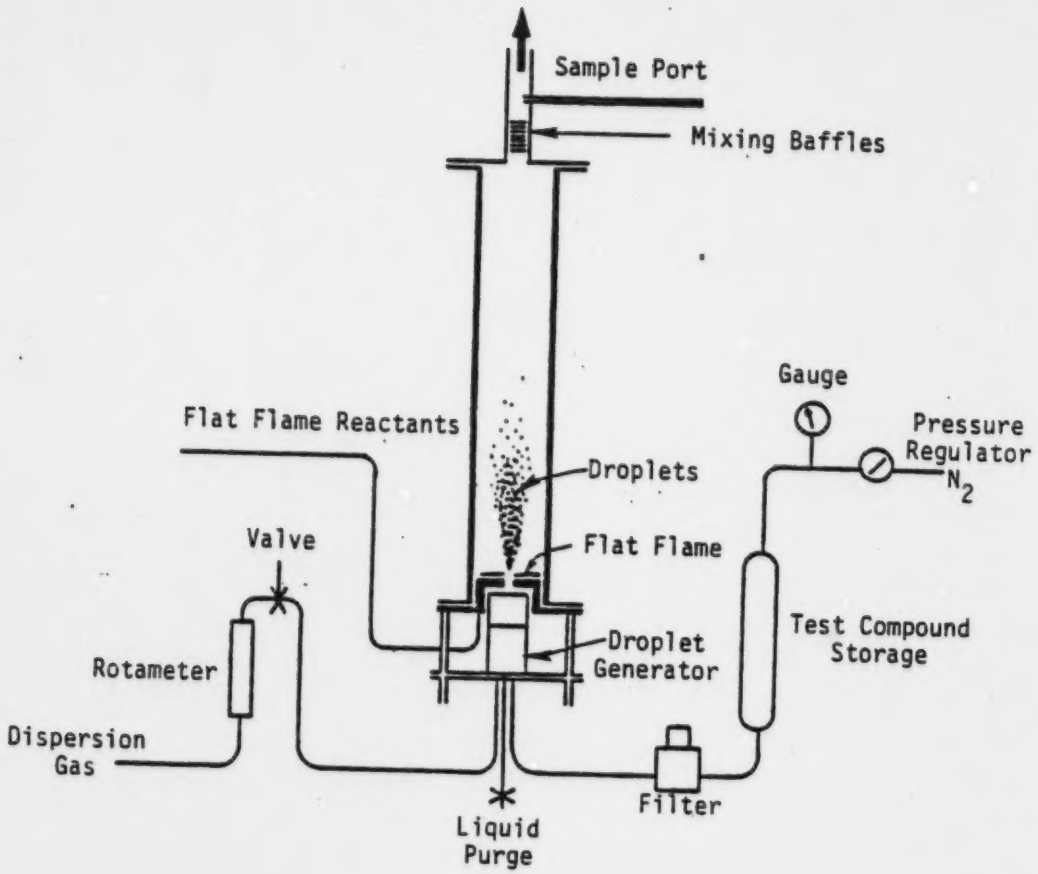


Figure 13. Microspray reactor.

- To compare flame (microspray) vs. non-flame (thermal decomposition) destruction on a fundamental level without the complicating influence of turbulence.

• Turbulent Flame Reactor

The turbulent flame reactor (Figure 14) was to provide a turbulent liquid spray flame, including swirl, recirculation, broad droplet size distribution, and high variation in droplet number density. The reactor was capable of simulating the compound escape mechanisms that could occur in flame zones of liquid injection incinerators. Very high heat removal rates were utilized to quench post-flame reactions. Thus, the destruction which occurred in the turbulent diffusion flame was emphasized over any non-flame decomposition which could occur in the post-flame region.

▲ Study Conclusion

• Under optimum conditions, flames are capable of destroying hazardous waste compounds with very high efficiencies (greater than 99.995 percent) without the need for long residence time, high-temperature post-flame zones or after-burners.

• Reduced flame destruction efficiencies are the result of operation under some failure mode such as poor atomization, poor mixing, or flame quenching.

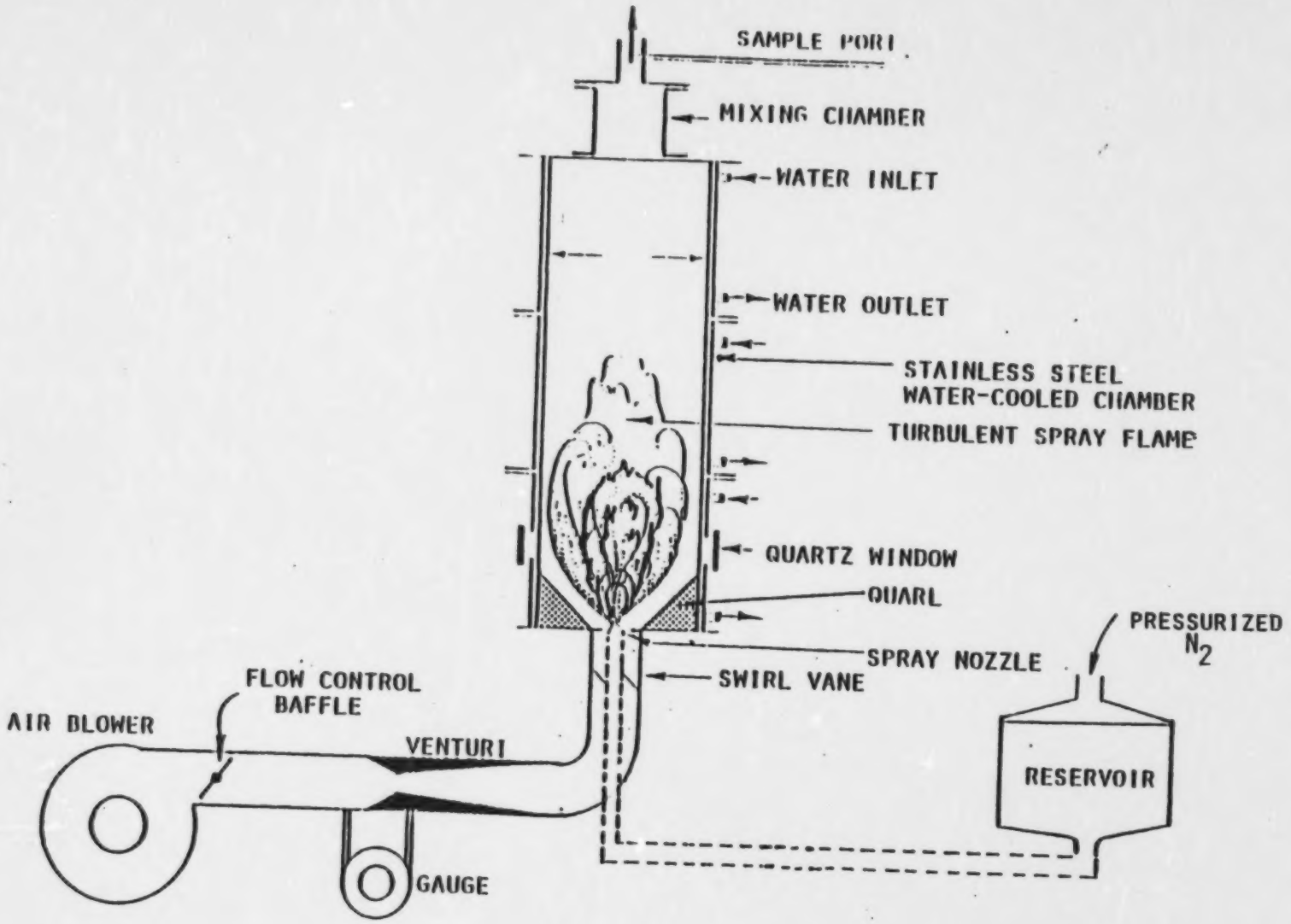


Figure 14. Turbulent flame reactor.

- Optimum conditions for destruction of hazardous waste compounds in turbulent diffusion spray flames correspond to minimal concentrations of CO and total hydrocarbons in the exhaust.

- Incinerability, or ordering of compounds in terms of their relative destruction efficiency, is dependent on the actual failure condition which caused the inefficiency. [It should be mentioned here, however, that the data set upon which this conclusion was reached is quite limited.]

- No one incinerability ranking system appears to predict correctly the relative destruction efficiency of the five compounds tested for all failure conditions investigated. However, several rankings did correctly predict relative destruction efficiency for specific failure conditions.

Thermal Destruction of Chlorophenol Residues

Study Scope

Environment-Canada conducted this research[31] to study the thermal decomposition phenomena of chlorophenol which the Canadian wood industry is using for wood protection/preservation. The specific objectives of their study were:

- To determine the effect of temperature and residence time on the thermal destruction of chlorophenols.

- To determine the relationship between the process characteristics applicable to the destruction of pure compounds and complex industrial mixtures such as wood preservation liquids and contaminated sludges.

- To estimate the products of incomplete combustion from chlorophenols destruction.

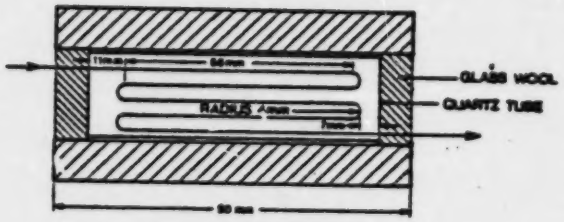
- To evaluate the feasibility of thermal elution technology as an analytical protocol.

▲ Study Approach

The experimental reactor used was similar to what was used by UDRI and Union Carbide Corporation. Figures 15 and 16 show the reactor and its flow diagram respectively.

The compounds were evaluated in order of increasing complexity of thermal destruction, beginning with pure compounds and then continuing with wood preserving mixtures and contaminated sludges. During the work with pure compounds, the thermal destruction characteristics including destruction efficiency

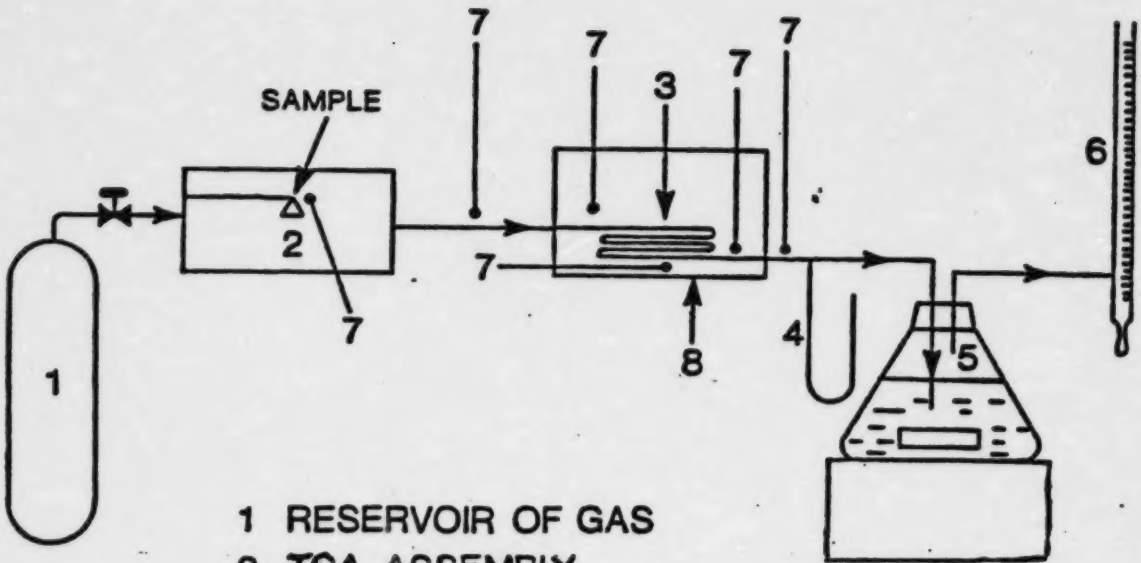
HIGH TEMPERATURE REACTOR



REACTOR SPECIFICATIONS

Total Length of the Reactor:	398 mm
Inside Diameter of the Reactor:	2 mm
Length to Diameter Ratio:	196
Material of Construction:	Quartz
Volume of Reactor:	1.25 mL

Figure 15. High temperature reactor and its specifications.



1 RESERVOIR OF GAS
2 TGA ASSEMBLY
3 QUARTZ REACTOR IMMERSED IN HIGH TEMPERATURE ZONE
4 MANOMETER
5 ABSORPTION TRAP
6 BUBBLE GAS FLOW METER
7 THERMOCOUPLE
8 FURNACE

Figure 16. Experimental equipment.

and PIC's were determined as a function of temperature and retention time (time interval during which the molecule was exposed to high temperature).

Testing was done in a non-flame mode oxidative environment in two steps: the compound was gradually vaporized and then passed through a high temperature zone with an excess of oxygen in order to avoid the possibility of pyrolytic reactions.

Vaporizing the sample prior to the thermal destruction ensured that the individual molecules were exposed to the actual destruction temperature in the chamber.

The data developed during the work with the pure compounds were utilized to predict the appropriate conditions for the work with the complex compounds.

All the laboratory thermal study work was designed to determine the relative importance and limits of effectiveness of the individual process variables required for safe disposal of chlorophenols in industrial situations.

Pure compounds of pentachlorophenol (PCP), 2,3,4,5 tetrachlorophenol, 2,4,6 trichlorophenol and 2,4,5 trichlorophenol (TCP) were tested and the decomposition thermograms of PCP and 2,4,5 TCP are given in Figures 17 and 18 respectively.

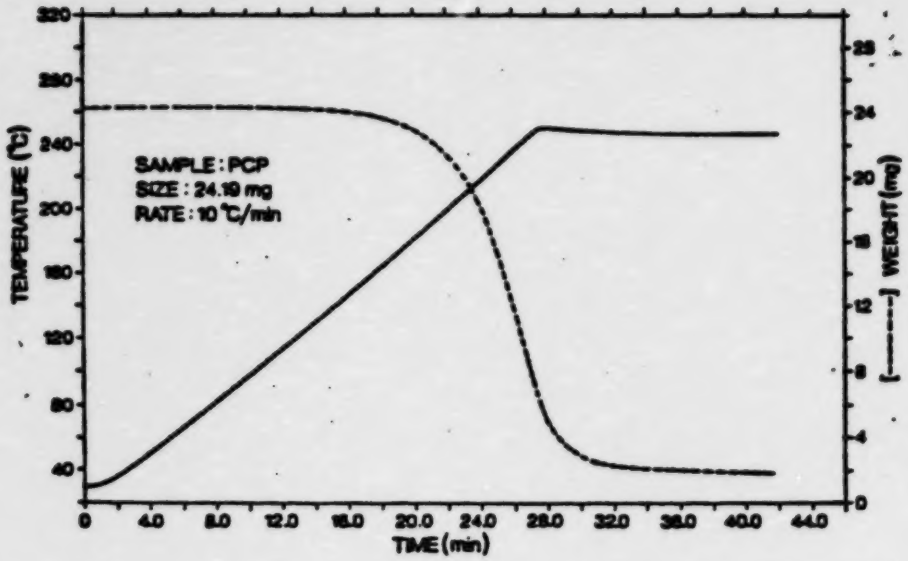


Figure 17. PCP decomposition thermogram.

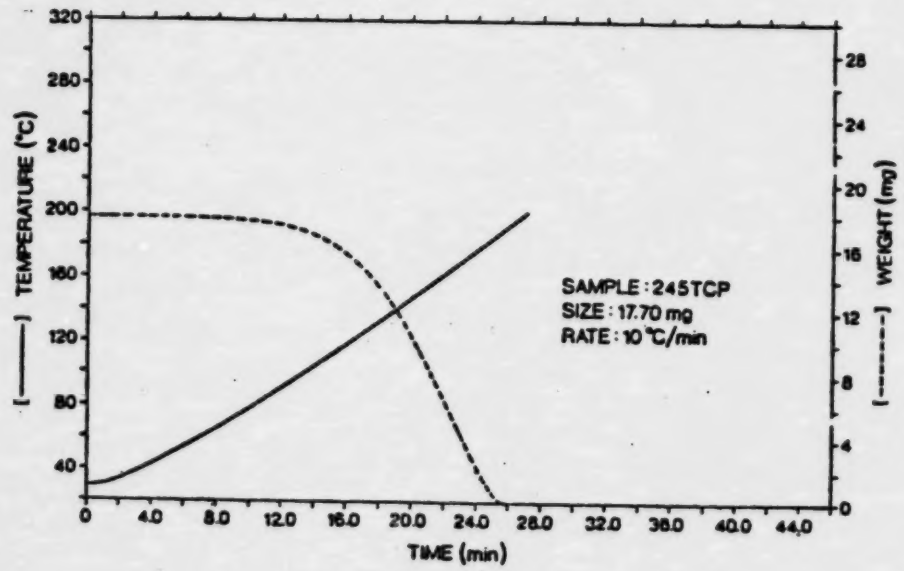


Figure 18. 2,4,5 TCP decomposition thermogram

Two wood preserving compounds, Alchem 4135 (supplied by Alchem Limited, Burlington, Ontario) and Woodbrite 24 (supplied by Van Waters and Rogers Ltd, Richmond), were investigated at their air-dried solid conditions. The chlorophenol content of ALCHEM 4135 and WOOD BRITE 24 is as follows:

	ALCHEM 4135	WOOD BRITE 24
Pentachlorophenol (%)	13.4	19.4
Tetrachlorophenol (%)	38	48

The destruction thermograms of these two compounds are shown in Figures 19 and 20 respectively.

The products of incomplete combustion of chlorophenols include lower chlorinated chlorophenols and more importantly, dioxins and furans. Identification of dioxins and furans as products of incomplete combustion is complicated by the fact that most commercial-grade chlorophenols and wood preserving fluids contain dioxin and furans as impurities in the basic formulations.

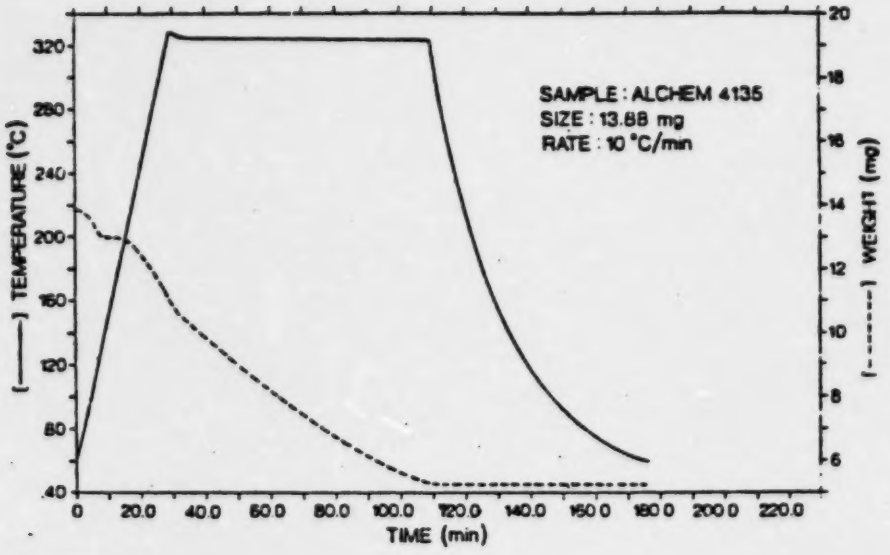


Figure 19. ALCHEM 4135 decomposition thermogram.

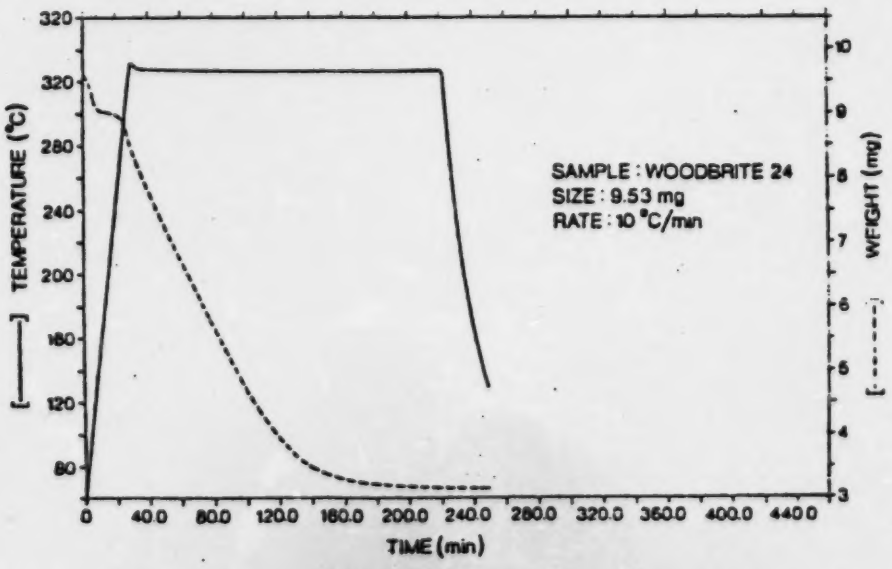


Figure 20. WOOD BRITE 24 decomposition thermogram.

▲ Study Conclusion

- A system capable of studying thermal decomposition of toxic compounds under laboratory conditions has been developed. The system is able to assess the basic parameters of decomposition at a relatively modest cost. Precise thermal regimes can be maintained within the system and minimal environmental risks are involved in the laboratory experimentation. Pure compounds, industrial mixtures and contaminated residues in both solid or liquid states can be assessed.

- Data developed in the laboratory system can be extrapolated beyond the limits of the equipment precision (99 percent destruction efficiency), when appropriate kinetic modelling techniques are applied. For example, based on the pure chlorophenol destruction data, it is estimated that at 900°C a gas residence time not exceeding 2.9 seconds is needed to ensure complete (>99.99 percent) destruction of both tetrachlorophenol and PCP whereas extrapolated data for 2,4,5 TCP show a residence time in excess of 5 seconds would be required.

- Significant amounts of dioxins and furans have been produced during the thermal destruction of chlorophenols at 700°C. At 900°C, similar quantities of dioxins and furans were detected, with the exception of trichlorodibromodioxin which appeared to

have been destroyed. Nevertheless, the concentration of highly toxic dioxins is very significant and should be of major environmental concern.

CURRENT RESEARCH ACTIVITIES

Hazardous Waste Incineration (HWI) Engineering Analysis

▲ Research Scope

- To predict the impact of changes in waste compositions and operating conditions on incinerator performance such as destruction efficiency and PIC formation.

- To extrapolate performance data from trial burns or field tests to predict the performance of similarly designed units.

- To extrapolate performance data from smaller scale to larger scale thermal destruction devices.

- To analyze the susceptability of a design to different failure modes and to predict their impact on incinerator performance.

▲ Research Approach

The research approach, as shown in Figure 21, is to integrate both theoretical analysis and experimental results into predictive models so that the performance of incinerators can be predicted without trial burns.

The approach for the theoretical analysis is to use existing models (kinetic, fluid dynamics, heat transfer, etc.) to develop predictive equations that govern incinerator performance. These models/equations will also be useful in generating hypotheses for performing future experimental work. The experimental approach is to conduct laboratory-, pilot- and full-scale testing to verify the applicability of the predictive hypotheses assumed. All results of EPA experimental projects will be analyzed for achieving this project goal.

It is expected that the two approaches, theoretical and experimental, will be continuously modified, and evaluated until sound models are developed and the objectives of this project are met.

The relationship of this project to EPA's ongoing experimental research studies is depicted by the following:

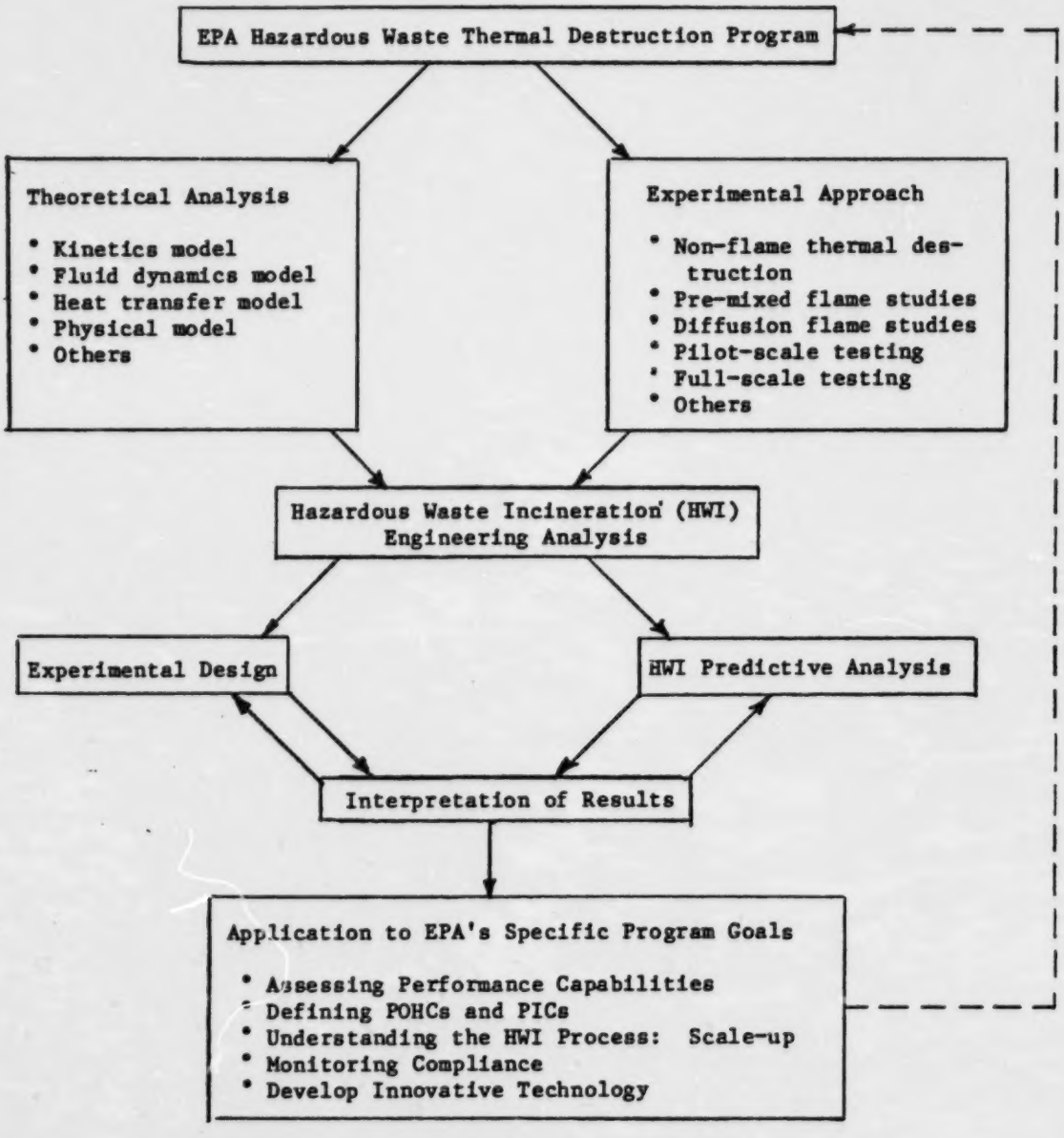
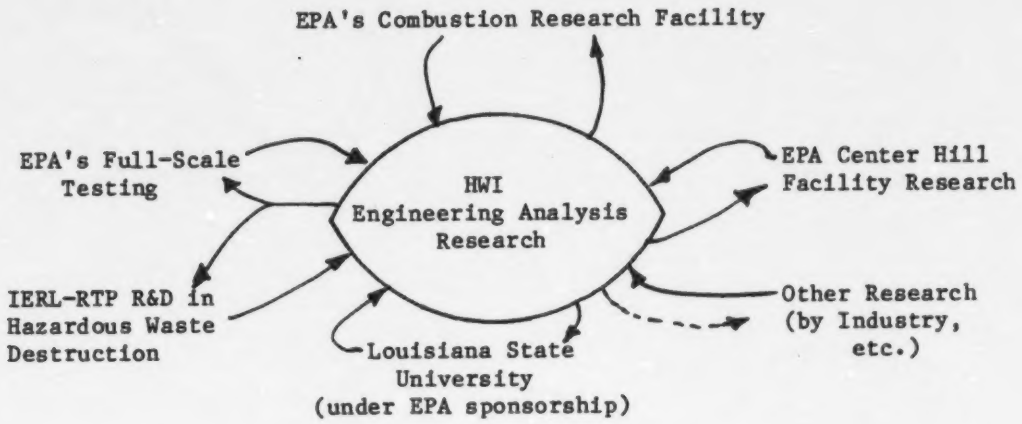


Figure 21. Approaches for the Hazardous Waste Incineration Engineering Analysis Project


EPA's Combustion Research Facility
EPA's Full-Scale Testing
HWI Engineering Analysis Research
EPA Center Hill Facility Research
IERL-RTP R&D in Hazardous Waste Destruction
Other Research (by Industry, etc.)
Louisiana State University (under EPA sponsorship)

▲ Research Status

This project was initiated in April 1984. The contractor, EERC, is currently developing the framework of the overall hazardous waste engineering analysis concept and the approaches to continuously monitor the performance of incinerators.

EPA In-House Thermal Destruction Research

▲ Research Scope

To supplement its extramural research, EPA has constructed both pilot- and bench-scale combustors at the Center Hill Facility of EPA's Industrial Environmental Research Laboratory in Cincinnati, Ohio. The primary focus of this in-house research is to:

- Establish how combustion parameters and variables affect failure of a simulated hazardous waste incinerator or an industrial boiler that co-fires hazardous waste with conventional fuel to achieve 99.99% DRE (Destruction and Removal Efficiency);

- Determine how, when and why PIC's are formed (e.g., too low an oxygen concentration or too low an operating temperature) and to determine how or whether they can be subsequently destroyed or removed (e.g., by secondary combustion or scrubbing/adsorption techniques); and

- Determine which organic chemicals are the hardest to burn (this will assist in making better POHC selections).

Research Approach

Four experimental systems will be utilized; they are:

- Thermal Destruction Unit-Gas Chromatographic (TDU-GC) System

The heart of the system is similar to UDRI's TDU-GC unit and is illustrated in Figure 22. The system has a quartz tube within an electrically heated tube furnace. The tube is designed to act as an isothermal plug-flow simulator. Dilute mixtures of test compounds are prepared in a preheated dilution chamber. Solids and liquids are vapor-

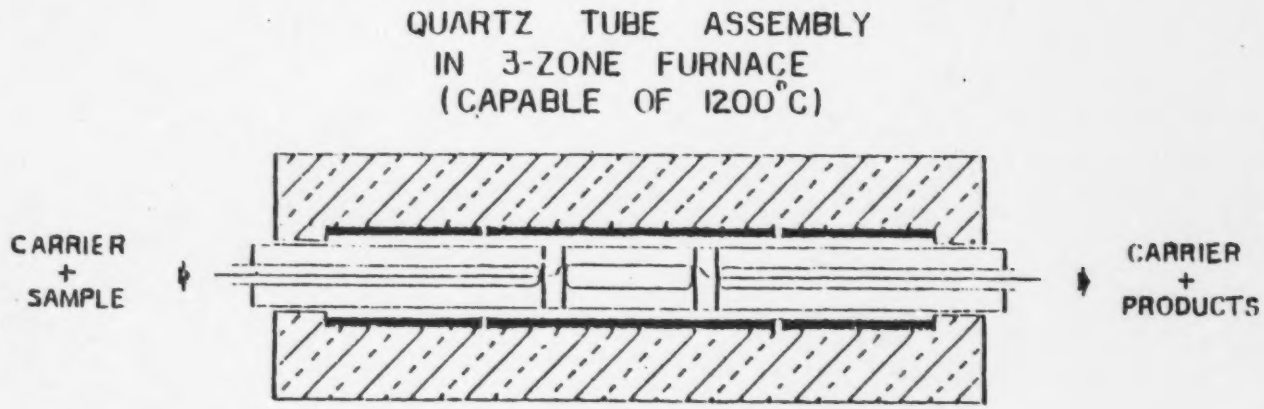


Figure 22. Sectional view of the TDU-GC furnace assembly.

ized in the chamber. The dilute mixture is inserted into the carrier gas stream at the upstream end of the quartz tube. The slug of dilute compound moves through the reactor and the extent of reaction is determined by comparing the measured concentration at the exit of reactor with the concentration when the furnace is cool enough to avoid reaction. The reactor effluent is normally analyzed by GC, occasionally by GC-MS (which permits detailed identification of PICs), or by GC-FID.

This system can be used to conduct research in many areas such as:

- Non-flame global destruction kinetics
- PIC formation in non-flame environments
- Compound incinerability comparison

- Microspray Reactor
- Turbulent Flow Reactor

} These two reactors are similar to what EERC used in their study (as described earlier in this Paper). Research activities on these two reactors will essentially continue and expand what has been done by EERC.

- Controlled Temperature Tower (CTT)

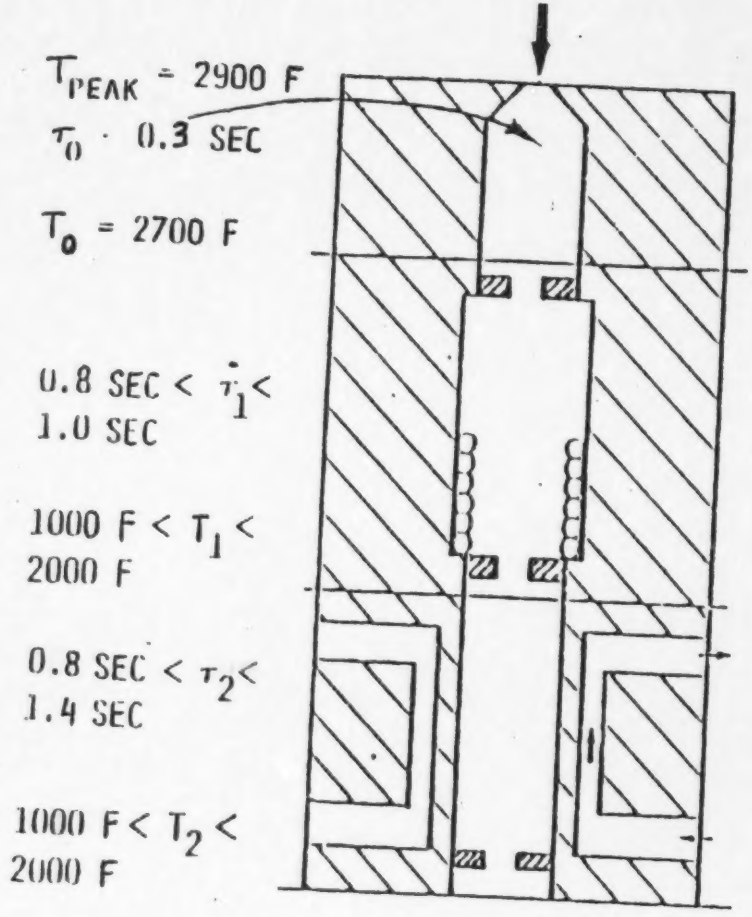
This unit was designed to allow simulation of a variety of incinerator thermal environments. A flame is established at the entrance to the reaction tunnel. The tunnel consists of three segments:

- In the flame zone, the tunnel is refractory-lined. The main flame is typically a swirl-stabilized turbulent spray flame. A variable swirl-block research burner is available that allows testing nominally at 150,000 Btu/hr.

- The second section is equipped with cooling coil access. Thus, the heat extraction rate can be varied by changing the amount of cooling coil surface exposed ranging from no heat removal to very high removal (to provide extreme thermal quench rates).

- In the third section, the wall is auxiliary-heated to reduce losses from the furnace gases. The degree of back-heating provides various thermal profiles in this third section.

The apparatus is shown in Figure 23 under the normal operating setup. Other reactant streams can be injected at the chokes to simulate staged combustion, secondary waste injection, or afterburner operation. The CTT has substantial flexibility for the simulation of incinerator behavior at small pilot-scale. For example, it can be used for pilot-scale verification of CO and THC as failure indicators.



- CHOKES IN
- FLAME ZONE COOLING AS DESIRED
- BACKFIRE ZONE AS DESIRED TO DETERMINE TEMPERATURE
- EXHAUST COOLING IF NEEDED

Figure 23. Schematic of Control Temperature Tower for Normal Operation.

▲Research Status

All four experimental systems described above and a scrubber system have been installed and are ready for shakedown testing. Personnel responsible for operating these units are currently preparing testing protocols and performing QA/QC activities.

Investigation of Gas-Phase Thermal Decomposition Properties of Hazardous Organic Compounds.

Under EPA's support, the University of Dayton Research Institute (UDRI) will continue their investigation of non-flame thermal decomposition phenomena.

▲Research Scope

In accordance with the work plan submitted to EPA, UDRI's current research objectives are to perform:

- Kinetics of Radical Attack
- Factors Affecting High Temperature Gas-Phase Thermal Decomposition
- Measurement of the Thermal Stability of POHCs and the Formation of PICs

▲Research Approach

The research approach is similar to what UDRI has been using in conducting their previous activities as described earlier. The emphasis is to continue testing of chemical compounds utilizing their extensive instrumentation.

▲Research Status

This phase of the UDRI research has just gotten underway. In completing their previous effort, UDRI has just submitted a draft report for EPA review[22]. The report covers the non-flame thermal destruction results of 20 test compounds.

The Incineration Characteristics of Selected Chlorinated Hydrocarbons (CHC)

As an EPA Center of Excellence, the Louisiana State University at Baton Rouge, has been conducting the fundamental studies relative to the incineration characteristics of selected chlorinated hydrocarbons since 1982[32,33]

Research Scope

- To develop information concerning high temperature combustion kinetics of organic hazardous waste compounds.

- To develop a better understanding of the chemical kinetic phenomena which occurs during the incineration of selected hazardous waste streams such as chlorinated methanes.

- To compare the results of CH_3Cl flames with those of CH_2Cl_2 and CCl_4, to study possible PICs in these flames and to study CO formation and two-stage reactions in chlorinated-loaded flames.

Research Approach

- Shock Tube

A stainless steel shock tube was employed (Figure 24) to study the ignition delay time for measuring the incinerability of CHC. The ignition delay time was defined as the time interval from the arrival of the shock at the end of the tube until the sudden rise in pressure due to the onset of the principal reaction exothermicity.

In the operation of a shock tube, a one-dimensional shock wave was caused to propagate within a tube filled with a potentially reactive gas

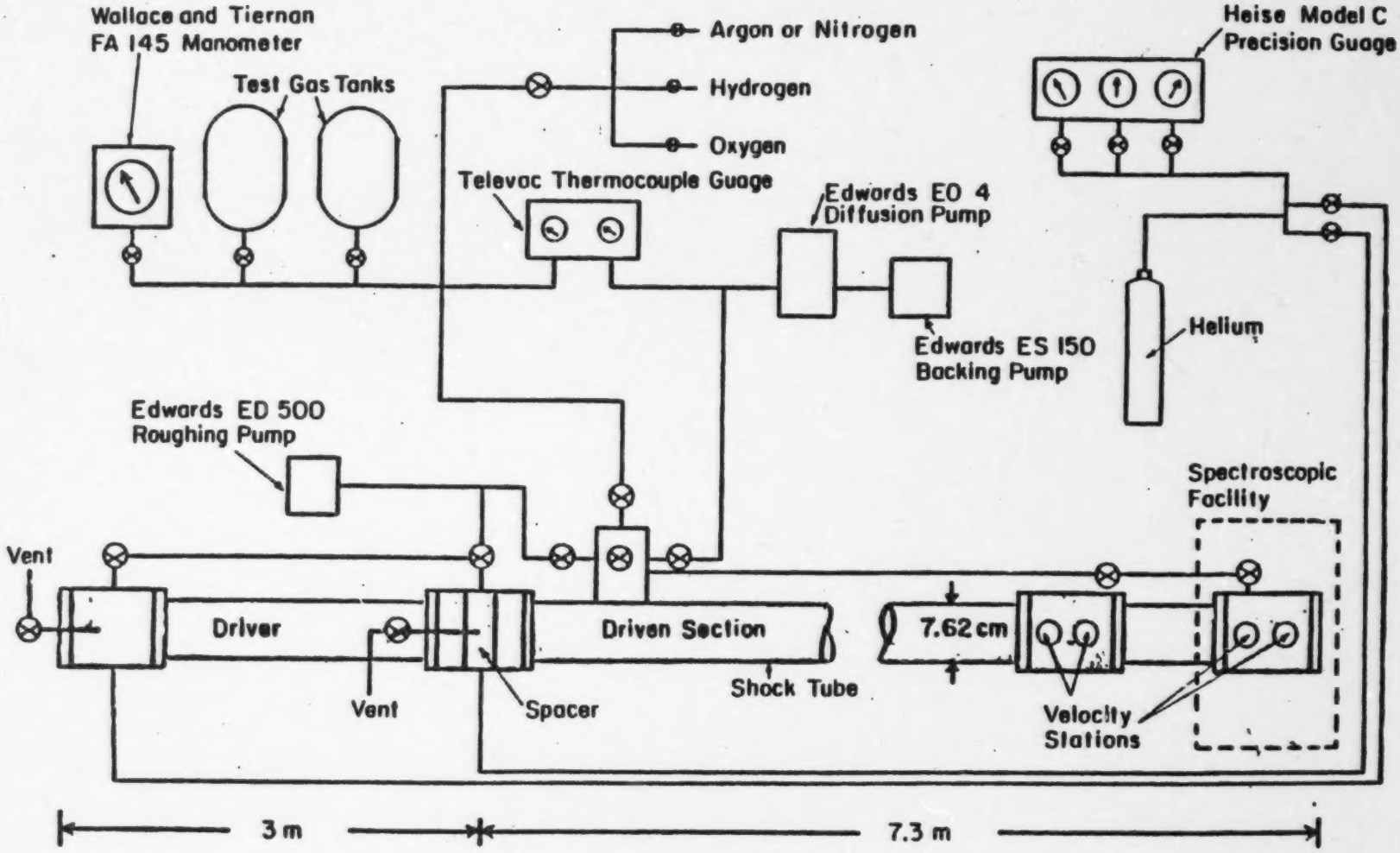


Figure 24. A schematic diagram of the conventional shock tube facility.

sample. This shock wave compresses the gas sample, thereby, heating the sample to a temperature high enough to initiate reactions.

Any gas-phase compound including pure hazardous waste compounds, with or without oxidizer, can be studied in this shock tube.

The passage of the shock wave through the experimental gas is equivalent to moving the gas from a reactor at room temperature to another reactor at a specified high temperature in a time on the order of 10^{-10} seconds.

The typical reaction time in a shock tube (2 milliseconds) is far shorter than the time for chemical species to diffuse to the walls and hence wall effects are negligible, according to the LSU scientists.

Compounds/mixtures tested were (1) methane and its chlorinated derivatives (2) ethane, 1,1,1-trichloroethane, and 1,2-dichloroethane, (3) ethane and trichloroethane, and (4) benzene and monochlorobenzene.

Ignition delay time data obtained were fit by least square analysis to an expression of the form:

$$\ln t = \ln A + (E/RT)$$

where

t = ignition delay time (micro-second)

R = universal gas constant (Cal/gm-mol-K)

T = limited experimental temperature (K)

A, E = empirical constants calculated by least square analysis

The test results disclosed that it was no more difficult to ignite the chlorinated hydrocarbons than their analogous hydrocarbons. This fact seems to agree with that of bond dissociation energy. The bond dissociation energy of C-H (415 KJ/mol) and C-Cl (280KJ/mol) indicates that chlorinated compounds will more readily decompose to produce the radical pool required to initiate ignition, the researchers at LSU contend.

Current efforts are focussed on the spectroscopic study of the apparent inhibition of the carbon monoxide conversion to carbon dioxide during the oxidation of CHCs. Future research direction will include the use of a single pulse shock tube to study the product distributions from the pyrolysis, oxidation and reduction of selected CHCs.

* One Dimensional Premixed, Laminar Flame Facility

The heart of this testing facility is the flame burner (Figure 25). The burner has a 6.0 cm diameter, sintered, porous stainless steel plug with heating/cooling coils embedded in it. The flames are shrouded from possible entrainment effect by passing a concentric nitrogen (N_2) shield gas around the flame holder through a bronze porous plug of 6.6 cm diameter. A 75 micro mesh screen is placed 6.2 cm above the burner to improve flame stability. The burner assembly which is housed within a 15.2 cm. Pyrex tube is supported by a 28.6 cm. diameter Teflon® rod.

The stoichiometric reaction equation for a general chlorinated hydrocarbon, $C_xCl_yH_z$, mixed with CH_4 and air is given by:

$$CH_4 + (R)C_xCl_yH_z + (2+R(4x-y+z)/4)O_2 \longrightarrow$$
$$(1+xR)CO_2 + (yR)HCl + (2+R(z-y)/2)H_2O$$

where R is the molar ratio of $C_xCl_yH_z$ to CH_4 which is used as fuel. This equation assumes the maximum conversion of H^- and Cl^- to HCl with any remaining Cl^- assumed to form molecular chlorine (Cl_2) and any remaining hydrogen assumed to form H_2O.

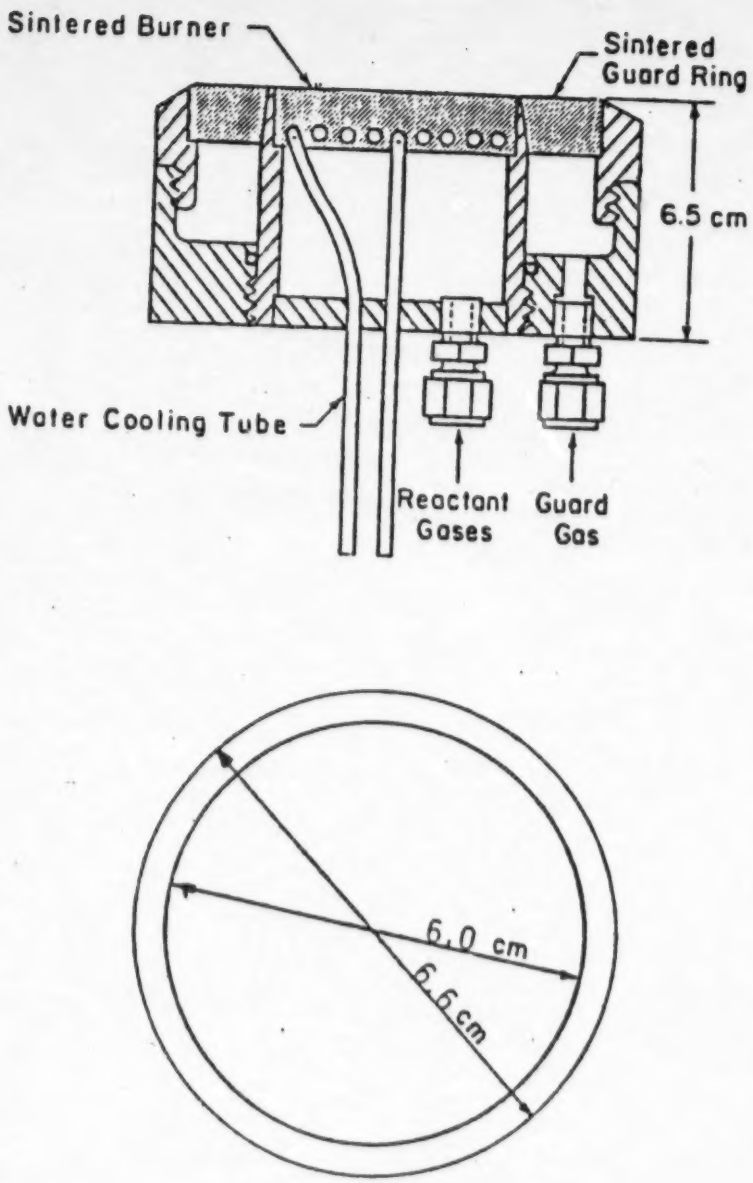


Figure 25. The Holthius Flat Flame Burner.

Compounds tested on this unit were CH_3Cl, CH_2Cl_2 and CCl_4. Both CH_2Cl_2 and CCl_4 are liquid at standard conditions.

The batched stable specie samples were analyzed on a Varian VISTA 6000 Gas Chromatograph (GC). The GC was equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) as well as a Varian VISTA 402 Data Analyzer for peak integration.

Major results, so far, are the findings of stable, hazardous intermediate compounds such as vinyl chloride (C_2H_3Cl) and dichloroethene $C_2H_2Cl_2$ during the flame-mode decomposition of CH_3Cl, CH_2Cl and CCl_4.

In the future, work will continue on all of the chlorinated methanes. Analytical requirements including EPA Method 601 are currently under test to quantify CHCs and chlorinated methanes. Modeling work will be used to develop global kinetic representations of the flame-mode destruction of CH_3Cl.

Non-Flame Waste Decomposition of Hazardous Waste

The Midwest Research Institute (MRI) has built a laboratory-scale unit to test gram quantities of hazardous waste in liquid, semi-liquid, or solid forms.

▲ Research Scope

- To predict optimum incineration operating conditions.
- To identify destruction efficiency as a function of time and temperature.

▲ Research Approach

A block-flow diagram of the system designed by Midwest Research Institute is shown in Figure 26.

Briefly, the MRI system consists of a volatilizing/pyrolysis heater containing the liquid or solid sample, and a second-stage incineration heater. This arrangement is parallel to actual incineration, in which the first stage vaporizes or pyrolyzes the feed material, with the vapors or gases passing into a second-stage combustion section that provides the required high temperature and residence time for their incineration. In this system, a sample of the waste material is inserted into a sample "boat" (in a hood) and pushed into the sample heater. Alternately, liquid can be continuously fed into the sample heater. The sample in that heater is volatilized or pyrolyzed, with the gaseous products being transported by a heated carrier gas (e.g., N_2). This gas then combines with heated flue gas, containing excess oxygen, after which it enters an incineration section (heater). Gas exiting the incineration heater passes through a sampling train for full-flow collection of samples for analysis.

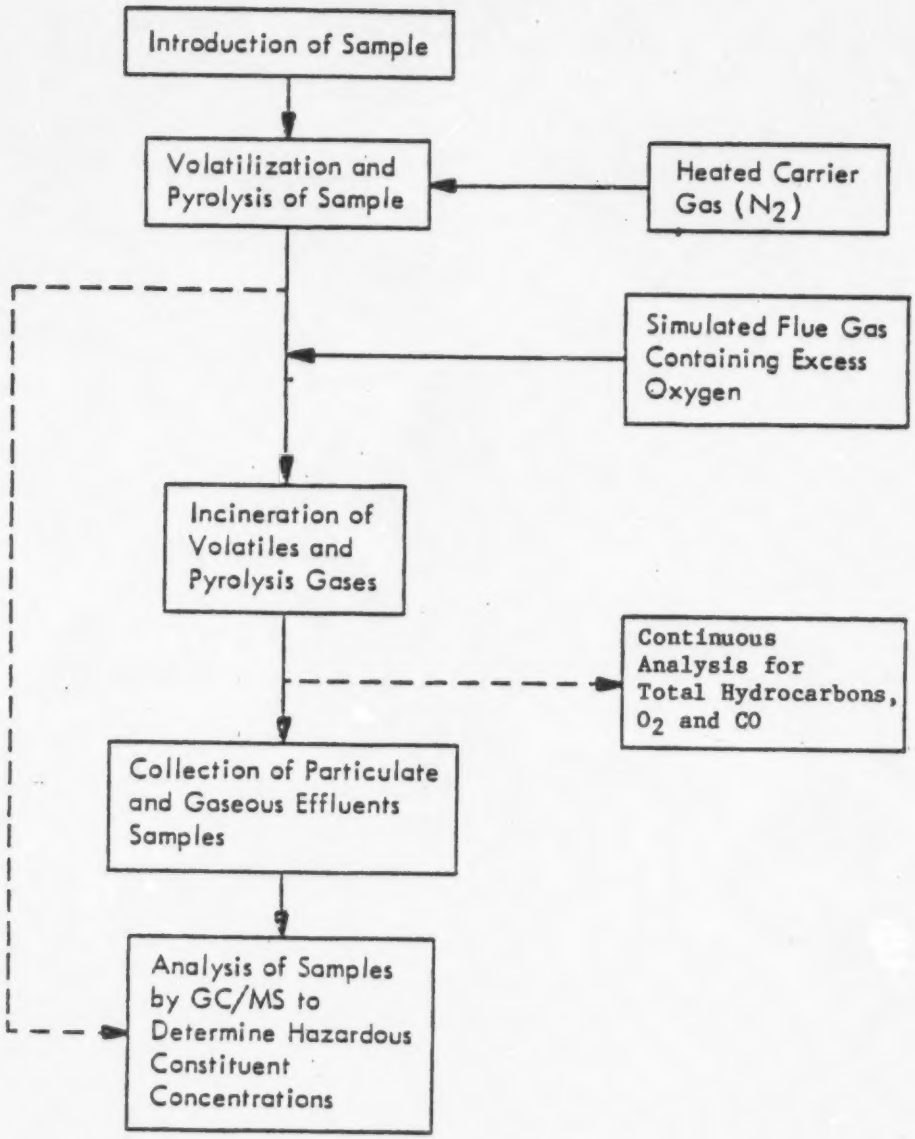

Introduction of Sample
Volatilization and Pyrolysis of Sample
Heated Carrier Gas (N_2)
Simulated Flue Gas Containing Excess Oxygen
Incineration of Volatiles and Pyrolysis Gases
Continuous Analysis for Total Hydrocarbons, O_2 and CO
Collection of Particulate and Gaseous Effluents Samples
Analysis of Samples by GC/MS to Determine Hazardous Constituent Concentrations

Figure 26. Block Diagram of Hazardous Waste Incinerator System

Major instrumentation contained in the system includes:

- Thermogravimetric analysis (TGA) to determine the temperature to which the material must be heated to completely volatilize/pyrolyze the sample.

- GC/MS to determine concentration of any hazardous organic constituents.

Compounds/waste tested or to be tested are:

- Solid hexachlorobenzene (HCB)

- Liquid hazardous waste composed of the following:

  - Trichloroethane
  - Tetrachloroethane
  - Bromodichloromethane
  - Pentachloroethane
  - Hexachloroethane
  - Dichlorobenzene

HCB tests have been conducted because HCB is a solid and also a surrogate for PCBs. The liquid waste is being used because it contains six compounds that may be difficult to incinerate since they have low heats of combustion.

The only available test results were from the HCB testing. The results show that:

POHC: HCB

% in waste feed: > 98 (solid reagent grade HCB used)

Temp.: 1000°C

Residence time: 0.3 sec

% DRE, Test 1: 99.972

% DRE, Test 2: 99.986

Average % DRE: 99.979

Heterogeneous Catalytic Oxidation of Model Chlorinated Hydrocarbons

Under an EPA Grant, Professor Michael P. Manning of the Massachusetts Institute of Technology is currently conducting this subject research.

Research Scope

- To examine methods for establishing the feasible and important engineering parameters in the heterogeneous catalytic oxidation of organic materials.

- To study the oxidation of model chlorinated hydrocarbons, based on the diverse chemical, physical, and stoichiometric composition of the hydrocarbons.

- To use the model compounds for the systematic investigation of the independent variable parameters such as bond type and order, degree of halogen substitution, and synergistic mixing effects for each of the catalysts.

Research Approach

An experimental apparatus (Figure 27) to measure the heterogeneous catalytic oxidation of chlorocarbons has been constructed.

The mixed feed stream flows to two split-tube furnaces placed in series. The first furnace functions as a preheater to bring the reactant gases up to the desired temperature. The second furnace is used to maintain the desired reaction temperature. The reactor is a glass-lined stainless steel tube, 4 mm I.D. The reactor portion of the catalyst tube is fitted into a solid aluminum cylinder to eliminate hot spots along the reactor wall. The tube is normally packed with about 2 cm^3 of sieved catalyst particles.

Gas samples of the reactor feed or product can be taken by opening the appropriate sample isolation valve and vacuum isolation valve. The vacuum pump then draws gas from the reactor tube through the sample loop of the gas sample valve in the chromatograph. When the vacuum isolation valve is closed, the pressure in the sample loop returns to the reactor operating pressure and the sample may be injected.

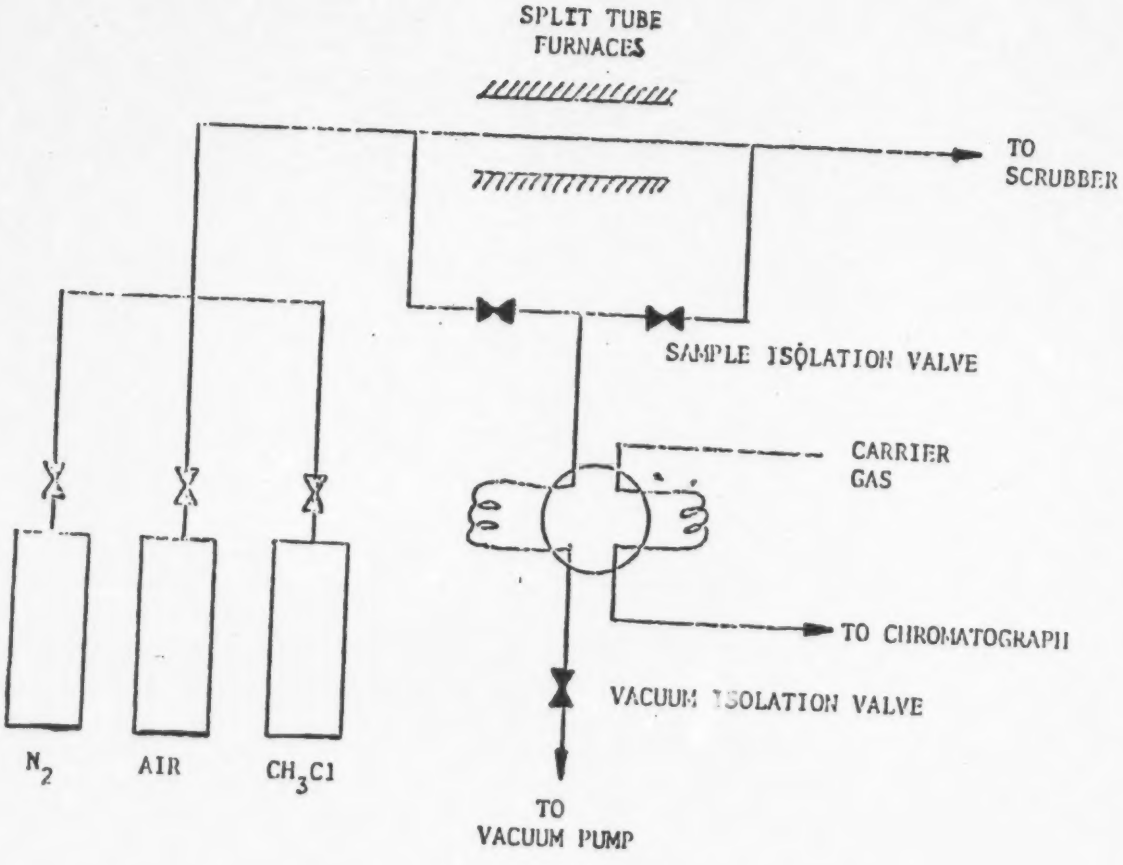


Figure 27. Reactor experimental flowsheet.

Exhaust gases from the reactor are normally bubbled through caustic to remove halogen and halogen acids and are then vented through a chemical fume hood.

The first catalyst tested was a commercial supported V_2O_5 sulfuric acid oxidation catalyst.

Preliminary experiments were carried out at temperatures of 360 and 412°C using inlet concentrations of 5% (mol) CH_3Cl in air. CH_3Cl and air were passed over the fresh catalyst for several hours before data was taken to allow the reaction and catalyst activity to reach steady state.

Visual inspection of the used catalyst showed a pronounced color change: the yellow-brown fresh catalyst had turned blue-green after exposure to CH_3Cl.

Preliminary study results were:

- A gas chromatographic analysis procedure for the quantification of feed and product streams of a chlorohydrocarbon oxidation reactor has been developed.

- Tenax-GC is capable of separating HCl, Cl_2, and H_2O among other species - a separation not previously reported.

- A commercially available, promoted V_2O_5 oxidation catalyst has been found to be inactive for the oxidation of methyl chloride below 420°C. This inactivity is most probably due to the temperature involved rather than halogen poisoning[34].

- Chromia-based catalysts, Cr_2O_3 supported on Al_2O_3, have been found to be effective for the oxidation of several chlorocarbons such as di, tri, and perchloroethylene[35].

Oxidation Of Model Waste Components In Supercritical Water

Supported by NASA, Professor Jefferson W. Tester of the Massachusetts Institute of Technology is conducting research relative to the reaction rates and mechanisms of waste destruction in the supercritical water environment.

▲ Research Scope

The overall goal of this research program is to understand the oxidation kinetics of model waste components in supercritical water. Reaction mechanisms in supercritical water are different from those in either low-pressure flame oxidation (combustion) or wet oxidation. Rate expressions from these other processes cannot be extrapolated a priori to conditions in supercritical water, as the supercritical water environment

is much different than combustion or wet oxidation environments. Information on the reaction rates and mechanisms in supercritical water is essential to accurately design and evaluate this process for destruction of wastes. The research is to help provide this information, identify any process limitation, and enable scale-up of laboratory results.

▲Research Approach

Oxidation in supercritical water is a new process for wastewater treatment, capable of almost complete conversion of toxic organics to carbon dioxide and water. Supercritical water, which is water above both its critical temperature of 374°C and critical pressure of 27.6 MPa (3200 psia), has much different physical properties than room temperature and pressure water and is an excellent media for oxidative reactions for several reasons. The high temperature of supercritical water promotes rapid reaction rates. Supercritical water also forms a miscible solution with air or oxygen, which eliminates the interphase mass-transport limitations that exist in a two-phase oxidation process[36]. Supercritical water has a lower density and dielectric constant than subcritical water, so that organics such as benzene which are partially soluble in room temperature water become completely miscible in supercritcal water[37], and inorganic salts such as sodium chloride readily precipitate from supercritical water[38]. The high solubility of organics in supercritical water promotes complete oxidation by preventing char formation from oxidation or decomposition by-products[39].

To reach the research goal of understanding kinetics in supercritical water, this research first determines rate expressions for pure components in supercritical water and then verifies these expressions for oxidation in multi-component mixtures. Currently, this research is investigating the oxidation of carbon monoxide and ammonia in supercritical water, as these steps may be the last and rate-limiting steps in the conversion of organic carbon to carbon dioxide and of organic nitrogen to molecular nitrogen.

The laboratory apparatus and experimental techniques were designed to be ideally suitable for determining accurate oxidation kinetics in supercritical water (Figure 28). The reactor is operated isothermally in plug flow, both of which are important to simplify the rate expression calculation. Isothermal conditions are maintained in the reactor by submerging it in a temperature-controlled, fluidized sand bath. The reactor is constructed of Inconel 625, which can withstand the high temperatures and pressures of the experiments. The reactor can be operated over a wide range of conditions, between 400 and 600°C and between 24 and 34 MPa (3500-5000 psia).

Within 18 months, experimental investigation of the oxidation of ammonia and carbon monoxide in supercritical water will be completed. Consequently, the orders of reaction for carbon monoxide, ammonia and oxygen, along with the activation energy and pre-exponential constant can be determined. An extensive review of the literature on oxidation

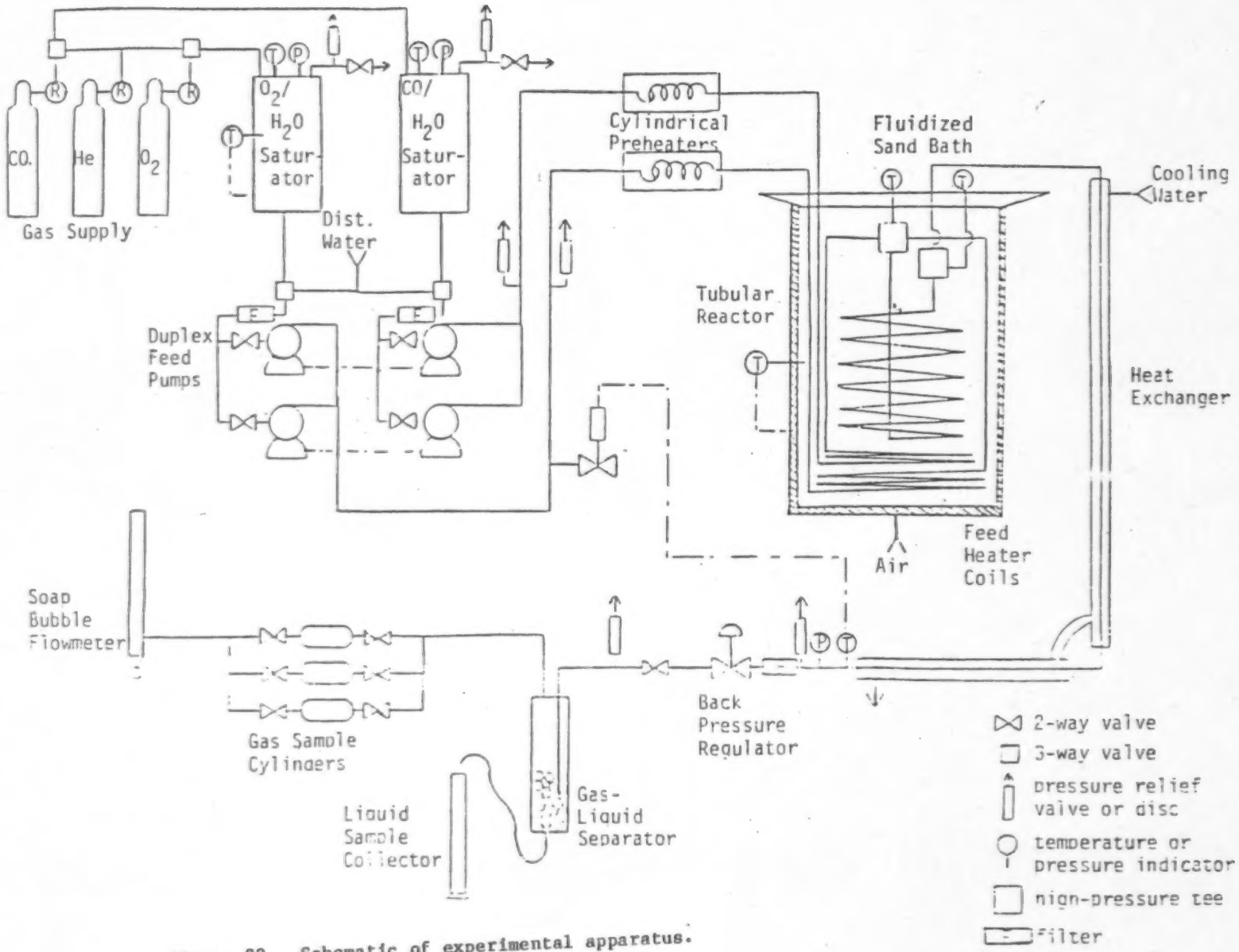


Figure 28. Schematic of experimental apparatus.

of carbon monoxide and ammonia under other conditions has been conducted. This review information will be compared to the experimental data to determine the applicability of results from other environments to supercritical water.

Molecular Beam Mass Spectroscopic Study of Chlorinated Hydrocarbon Flames

Under an EPA grant, Professor S. Senkan of the Illinois Institute of Technology is continuing his studies on the laminar flames of chlorinated hydrocarbons (CHC). Present research is aimed to develop a more detailed understanding of the chemistry of such flames and to develop more comprehensive models describing the CHC oxidation processes and to assess the formation and emission of pollutants from practical combustion incineration systems.

▲ Research Scope

- To study and characterize the complete chemistry of select chlorinated hydrocarbon flames as a function of adjustible variables such as the mixture equivalence ratio.
- To examine the formation and destruction of intermediates in the flames of select CHC species.
- To assess the formation and subsequent emission of pollutants from practical incineration systems.

▲Research Approach

Experiments are being carried out in a laminar flat flame burner similar in design to the system described earlier (see Figure 11). The flames are probed for the determination of species profiles using molecular beam sampling coupled with on-line mass spectroscopy (MBMS). The MBMS is a highly versatile method for studying reactive gaseous mixtures, because of its ability to furnish information on the presence of all stable and radical species in flames.

In parallel with the experiments, detailed chemical kinetic modeling of the flames are also being pursued.

CONCLUSION AND RECOMMENDATION

Table 3 presents an overall summary of who has tested which compounds. It shows:

- ▲ A list of compounds which have been studied by various institutes
- ▲ Temperatures at different destruction efficiency and residence time. Some of these data are actual test results and others are calculated values using correlations developed by Lee, et al.[24]. The temperature data seems to show that for aromatic ring structure compounds of the benzene group, the destruction

temperature increases with increasing chlorine substitution. However, for straight bond, paraffin compounds, such as methane, ethylene, and ethane, there is no temperature pattern with respect to the substitution of chlorine. The table also shows that acetonitrile requires the highest temperature, 950°C, to reach 99.99% destruction efficiency, and triethylamine requires the lowest temperature, 570°C to reach the same level of destruction efficiency.

- Observed PIC compounds. Table 3 appears to show that combustion of chlorinated phenols requires special care, because they can produce dioxin and furan as PICs.

- Although Table 3 shows that compounds at full range of heat of combustion can be destroyed to meet 99.99% DRE under 1000°C temperature, the PICs information is very limited. Because PICs could be more hazardous than the original compounds, studying PIC formation and control should be one of the most important research areas that EPA should focus on.

- Because many compounds are suspected to be PICs of one another, it is suggested that, for those who must determine POHC's for trial burns, compounds should be selected with different structures to minimize the possible formation of the same PICs from selected POHCs.

Table 3. SURVEY OF HAZARDOUS WASTE THERMAL DESTRUCTION TEST RESULTS

COMPOUND		Study Institute**	T99/2**°C	T99.99/2**°C	PIC
Acetonitrile (Methyl Cyanide)	CH_3CN	7,8		950[8]	
Acrolein	C_3H_4O	5	524		
Acrylonitrile	C_2H_4CN	2,7,8		703[7], 860[8]	
Allyl Alcohol	C_3H_5OH	7		581	
Allyl Chloride	C_3H_5Cl	7		649	
Ammonium Hydroxide	NH_4OH	5			
Aniline	$C_6H_5NH_2$	8		750	
Anthracene	$C_{14}H_{10}$	8	710		
Benzene	C_6H_6	2,3,4,7,8	730	717[7], 760[8]	
Chlorobenzene	C_6H_5Cl	2,3,4,7,8	690	744[7], 780[8]	
1,2-Dichlorobenzene	$C_6H_4Cl_2$	6,8	740	780	
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	8	750	790	
1,2,3,4-Tetrachloro-benzene	$C_6H_2Cl_4$	8	760	850	
Pentachlorobenzene	C_6HCl_5	8	810		
Hexachlorobenzene (HCB)	C_6Cl_6	2,7,8	810	880	
Nitrobenzene	$C_6H_5NO_2$	8		700	
Pentachloronitrobenzene	$C_6Cl_5NO_2$	8	590		HCB
Benzo(e)pyrene	$C_{20}H_{10}$	8	720		
Biphenyl (Polychlorinated Biphenyls)	$C_{12}H_{10}$	8	700*		
Aroclor 1221	$C_{12}H_{8.8}Cl_{1.2}$	8	740*		

**See the key at the conclusion of this Table.

Table 3. SURVEY OF HAZARDOUS WASTE THERMAL DESTRUCTION TEST RESULTS - Continued

COMPOUND		Study Institute	T99/2,°C	T99.99/2,°C	PIC
Aroclor 1232	$C_{12}H_{8.1}Cl_{1.9}$	8	740*		
Aroclor 1242	$C_{12}H_{6.9}Cl_{3.1}$	8	740*		
Aroclor 1248	$C_{12}H_{6.1}Cl_{3.9}$	8	740*		
Aroclor 1254	$C_{12}H_5Cl_5$	8	740*		
Aroclor 1260	$C_{12}H_{3.7}Cl_{6.3}$	8	740*		
Aroclor 1262	$C_{12}H_{3.2}Cl_{6.8}$	8	740*		
2,6-Dichlorobiphenyl	$C_{12}H_8Cl_2$	8	800		Chlorinated benzenes, chlorinated benzofurans, & other PCBs
2,5,2',5'-Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	8	740		
2,5,2',4',5'-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	8	820		
2,2',4,4',5,5'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	8	730*		
Decachlorobiphenyl	$C_{12}Cl_{10}$	8	780*		
2,2'-Dibromobiphenyl	$C_{12}H_8Br_2$	8	800		
Pentabromobiphenyl	$C_{12}H_5Br_5$	8	800		
2,2,4,4,5,5-Hexabromobipheyl	$C_{12}H_4B_6$	8	800		
Heptabromobiphenyl	$C_{12}H_3Br_7$	8	800		

Table 3. SURVEY OF HAZARDOUS WASTE THERMAL DESTRUCTION TEST RESULTS - Continued

COMPOUND		Study Institute	T99/2,°C	T99.99/2,°C	PIC
2,2,4,4,5,5-Hexabromo-biphenyl	$C_{12}H_4Br_6$	8			
Butane	C_4H_{10}	7		646	
Carbon Monoxide	CO	3,5			
DDE (1,1-Dichloro-2-(O-chlorophenyl)-2-(P-chlorophenyl) Ethylene)	$C_{14}H_8Cl_4$	8	790*		
DDT(Dichloro-diphenyl-trichloroethane)	$C_{14}H_9Cl_5$	8	480*		DDE
Diazinon	$C_{12}H_{21}N_2O_3PS$	8	560*		
Dioxin					
Dibenzo-p-Dioxin	$C_{12}H_8O_2$	8	840*		
2-Chlorodibenzo-p-Dioxin	$C_{12}H_7O_2Cl$	8	840*		
2,7-Dichlorodibenzo-p-Dioxin	$C_{12}H_6O_2Cl_2$	8	840*		
Trichlorodibenzo-p-Dioxin	$C_{12}H_5O_2Cl_3$	8	840*		

Table 3. SURVEY OF HAZARDOUS WASTE THERMAL DESTRUCTION TEST RESULTS - Continued

COMPOUND		Study Institute	T99/2,°C	T99.99/2,°C	PIC
Endrin	$C_{12}H_8Cl_6O$	8	400*		
Ethane	C_2H_6	2,4,7,8	600	720[7], 785[8]	
1,2-Dichloroethane	$C_2H_4Cl_2$	3,4,7	634[7]		
1,1,1-Trichloroethane	$C_2H_3Cl_3$	4,6,8		600[8]	
1,1,2-Trichloroethane	$C_2H_3Cl_3$	8			
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	6,8			
Pentachloroethane	C_2HCl_5	6			
Hexachloroethane	C_2Cl_6	8		640	
Ethanol	C_2H_5OH	7		680	
Ethyl					
Ethyl Acrylate	$C_2H_5CH_2CHOO$	7		589	
Ethylbenzene	$C_2H_5C_6H_5$	2,7			
Ethyl Formate	C_2H_5HCOO	7		619	
Ethyl Mercaptan	C_2H_5SH	7		808	
Ethylene	C_2H_4	2,7		694[7]	
Dichloroethylene	$C_2H_2Cl_2$	5			
Trichloroethylene	C_2HCl_3	3			
Tetrachloroethylene	C_2Cl_4	8		920[8]	
Perchloroethylene	C_2Cl_4	5			
Furan					
Dibenzofuran	$C_{12}H_8O$	8	700*		
2,8-Dichlorodibenzofuran	$C_{12}H_6OCl_2$	8	800		
Halowax	$C_{12}H_{4.5}Cl_{3.5}$	8	770		
Heptachloronaphthalene	$C_{10}HCl_7$	8	760		
Hexachlorobutadiene	C_4Cl_6	8	750	780	
Hexachlorocyclopenta-diene (HCCP)	C_5Cl_5	8	650		HCB

Table 3. SURVEY OF HAZARDOUS WASTE THERMAL DESTRUCTION TEST RESULTS - Continued

COMPOUND		Study Institute	T99/2,°C	T99.99/2,°C	PIC
Kepone	$C_9Cl_{10}O$	8	470*		HCCP & HCB
Methane	CH_4	2,3,4,7,8		808[7], 870[8]	
Methyl Chloride	CH_3Cl	3,4,7	770	824[7]	
Dichloromethane	CH_2Cl_2	3,4,8		780[8]	
Chloroform	$CHCl_3$	2,3,8	590	620[8]	Tetrachloroethylene & Pentachloroethane
Carbon Tetrachloride	CCl_4	4,8	760	820[8]	Vinyl chloride & dichloroethane
Bromodichloromethane	B_rCHCl_2	6			
Methyl Ethyl Ketone	$CH_3COC_2H_5$	7,8		675[7]	
Mirex	$C_{10}Cl_{12}$	8	680		HCB
Octachlorocyclopentene	C_5Cl_8 (OCCP)	8	460		
Phenol	C_6H_6O				
Chlorophenol	C_6H_5ClO	1		900	Dioxins & Furans
2,4,6-Trichlorophenol	$C_6H_3Cl_3O$	1		900	
Tetrachlorophenol	$C_6H_2Cl_4O$	1		900	
Pentachlorophenol	C_6HCl_5O	1		900	

TABLE 3. SURVEY OF HAZARDOUS WASTE THERMAL DESTRUCTION TEST RESULTS - Continued

COMPOUND		Study Institute	T99/2,°C	T99.99/2,°C	PIC
Dichlorobiphenol	$C_{12}H_4Cl_2O$	8			
Hexachlorobiphenol	$C_{12}H_4Cl_6$	8			
2,2'-Dibromobiphenol	$C_{12}H_8Br_2$	8			
Propane	C_3H_8	7		705	
Propylene	CH_3CHCH_2	7		675	
Pyridine	$N(CH)_4CH$	8		840	
1,2,3,4-Tetrachloro-naphthalene	$C_{10}H_4Cl_4$	8	760		
Toluene	$CH_3C_6H_5$	7		702	
Triethyl Amine	$(C_2H_5)N$	7		570	
Triphenylene	$C_{18}H_{12}$	8	720		
Vinyl Acetate	$CH_3COOCHCH_2$	7		629	
Vinyl Chloride	CH_2CHCl	7		723	

**KEY:

$T_{99/2}{}^{o}C$ = Temperature at 99% destruction efficiency and 2 second residence time.

$T_{99.99/2}{}^{o}C$ = Temperature at 99.99% destruction efficiency and 2 second residence time

* = Temperature at 99% destruction efficiency and 1 second residence time.

PICs = Products of incomplete combustion

Continued -

1 - Canadian Plug-Flow Simulator[31]

2 - Energy and Environmental Research Corporation Kinetic Calculations[28]

3 - Illinois Institute of Technology Flat-Flame Reactor[25,26,27]

4 - Louisiana State University Flat-Flame Reactor[33]

5 - Massachusetts Institute of Technology Supercritical Water and Catalytic Combustion

6 - Midwest Research Institute Non-Flame Reactor

7 - Union Carbide Plug-Flow Simulator[23,24]

8 - University of Dayton Research Institute Plug-Flow Simulator[22]

▲ Most data shown in this paper were obtained from non-flame and microgram-quantity testing environments. The credibility of these data for actual incineration under flame conditions remains to be demonstrated. Therefore, research is needed to determine the applicability of non-flame, and microgram-testing results to the full-scale realities of actual incinerators.

▲ Although there is a significant amount of experimental data, no analytical methods have been developed to predict what DRE or PICs would result if incinerator conditions change. Research is needed to fill that void.

As a conclusion of this paper, the technical review of laboratory- and bench-scale research shows that:

- POHC selection is not trouble-free;
- Incinerability rankings are not uniform; and
- PIC identification and control are critical issues remaining in hazardous waste incineration research.

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